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ADVANCES IN PHYSICS
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The Mineralogy of Rock Magnetism

By G. D. NICHOLLS
Lecturer in Petrology, University of Manchester

§ 1. INTRODUCTION

ROCKS are essentially aggregates of mineral grains. Some rock-forming minerals are diamagnetic e.g. quartz, felspar, some are paramagnetic e.g. pyroxene, biotite and a few are ferrimagnetic e.g. magnetite. The latter are usually designated, somewhat loosely, the ferromagnetic fraction. In the many studies which have now been made on the magnetic behaviour of rocks the natural magnetization has usually been attributed to the presence of a ferromagnetic fraction. By separating this fraction from rocks of high susceptibility Jouravsky, Charczenko and Choubert (1933) demonstrated that the natural magnetization could reasonably be attributed to the magnetite alone, and Koenigsberger (1938) similarly discussed his results in terms of the ferromagnetic minerals present in his specimens although clearly aware of the slight contribution made by the paramagnetics present. The practice is now generally followed (Akimoto 1951, p. 47, Nagata 1953 a).

Natural ferromagnetic minerals may be classified into two groups, the oxides and the sulphides. The oxides are usually more abundant than sulphides and, in consequence, have a greater influence on the magnetic properties of the rocks containing them. Frequently in discussions of rock magnetism the possible presence of sulphides is ignored although the ferrimagnetic sulphide, pyrrhotite, may be more widespread, especially in igneous rocks, than is generally supposed (Newhouse 1936).

The magnetite of rocks is variable in composition and a number of investigators (Michel 1937, Bénard and Chaudron 1937, Michel, Chaudron and Bénard 1951, Akimoto 1951 and 1954) have shown that the magnetic properties vary with change in composition in this mineral. To a considerable degree the intensity of saturation magnetization and Curie Point depend on the chemical composition of the mineral but certain other magnetic properties depend also on the size and shape of the mineral grains. Akimoto (1951) and Chevallier and Mathieu (1937) have demonstrated the dependence of magnetic susceptibility on grain size, the former for cubic ferromagnetics close to magnetite in composition and the latter authors for hematite. Gottschalk (1935) has reported a remarkable increase in the coercive force of magnetite when the grain size is reduced to approximately 20 μ and on examination of the ore minerals of various Japanese volcanic rocks Nagata (1953 a) found a general increase of coercive force with decreasing grain size. The magnetic properties of rocks may further depend on the amount and mode of occurrence of the ferromagnetics e.g. whether they form discrete grains or aggregates of two (or more) minerals of this type. Such aggregates or intergrowths are not uncommon in certain kinds of igneous rock, especially intergrowths of magnetite and the iron–titanium oxide, ilmenite. How far the magnetic behaviour of the rock will be influenced by the occurrence of the ferromagnetics in intergrowths depends on the conditions under which the intergrowths formed and the way in which the component minerals acquired magnetization. It is necessary, therefore, to consider the probable origin of any intergrowths present in any mineralogical studies accompanying investigations into the magnetization of rocks.

This paper reviews existing knowledge on these and allied topics.

§ 2. METHODS OF STUDY OF THE OPAQUE MINERALS

Many of the techniques employed in the study of thin sections of rocks and minerals in transmitted polarized light are of little or no value for the study of the ferromagnetic minerals since most of these are opaque except in exceedingly thin flakes and grains. Special techniques have therefore been adopted among which the following are important :—

1. Examination of polished sections of minerals, or the rocks containing them, by reflected light under an ore microscope.
2. Separation of the minerals from the host rock followed by
   (*a*) identification of phases present by x-ray powder photography,
   (*b*) thermo-magnetic investigations,
   (*c*) chemical analysis of the pure minerals.

1. Direct visual examination of the opaque ferromagnetic minerals in polished sections of the rocks may yield valuable information on the mode of occurrence of these minerals, the presence or otherwise of intergrowths, grain size and shape, and the number of different ferromagnetics present.

The general techniques of the preparation of specimens for examination by reflected polarized light have been described by Short (1948) and Hallimond (1953). A flat surface is prepared on the specimen by sawing off a fragment with a diamond saw. The fragment is then mounted in a resin, ground to a smooth surface with different grades of carborundum powder and finally polished on rotating laps to which a polishing abrasive is applied as a moist paste. In a study of naturally occurring opaque oxide ore minerals, Basta (1953) mounted his specimens in Marco Resin and ground them by hand using 303 grade emery on a phosphor bronze lap for soft minerals, or 600 carborundum on a cast-iron lap for the hard specimens. The average time for grinding was 20 minutes. His specimens were polished on a Cooke, Troughton and Simms ore polishing machine using spirally grooved plastic laps rotating at about 100 rev/min. The abrasive was added to the laps in the form of a suspension in water. For some magnetites he used graded rouge as the abrasive, for the harder ilmenites and magnetites chromic oxide, and for final polishing 'Gamma Alumina'. The average time of polishing was 90 minutes. The method produces surfaces of almost no relief.

The general techniques of examination of materials by reflected polarized light have been described by a number of authors (Schneiderhöhn and Ramdohr 1934, Schneiderhöhn 1952, Hallimond 1953, pp. 100–136). Hallimond's text is particularly valuable to British workers since it describes equipment readily available in Britain. Observations on the identity of the ferromagnetic ores has hitherto been largely qualitative—sulphides may be distinguished from oxides and cubic oxide minerals from those of rhombohedral crystallization, but there is at present a scarcity of information correlating properties of these materials in reflected light with chemical composition. Quantitative measurements may be made, e.g. of reflective power, defined as the ratio of intensity of light reflected from a given surface to the intensity of light vertically incident upon it, but they depend on the perfection of polishing during the preparation of the section and, in the past, figures from different laboratories have not always been in agreement. The recent introduction of graded diamond abrasives should remove many of the difficulties in the polishing process and lead to better agreement in the future. Direct measurement of reflective power can be made by visual comparison using a microphotometer (Hallimond, *op. cit.*, pp. 131–136, gives a description of this instrument and its use) or by means of an eyepiece in which the image can be projected upon a photocell. The former method is reliable and, by taking several readings, an accuracy of ± 1–2% is claimed for it. Photocells are more sensitive but require more attention to maintenance and calibration. With anisotropic materials, such as the rhombohedral oxide ore minerals, the reflective power varies with the direction of vibration of the polarized light relative to the orientation of the crystal lattice of the mineral under examination. For two directions at right angles the reflective power has maximum and minimum values, the difference being termed the bireflection of the material. This is a second quantitative value which may be used in the study of anisotropic minerals. The cubic group of ore minerals, being isotropic, do not exhibit bireflection—reflective power is independent of the vibration direction of the light relative to the crystal lattice. Reflective power may vary with the wavelength of incident light and should be determined for selected (and reported) wavelengths—filters transmitting bands approximately 20 mμ wide are generally used rather than light from a monochromator. A different value is obtained if this property is determined on a polished section covered with oil (oil of refractive index 1·52 is often used) instead of on a section examined in air. Further quantitative measurements may be made on anisotropic material (Hallimond, *op. cit.*, p. 180) but at present reference data is too scanty for them to be of any value in the quantitative estimation of composition in the rhombohedral series of ferromagnetic ore minerals. Colour of the minerals in reflected light may also be used for qualitative work. For anisotropic materials the directions of maximum and minimum reflective power may each show a characteristic colour so that upon rotation of such materials under polarized illumination a change in colour may be observed—called reflection-pleochroism. Etching tests have been used and Phillips (in Phillips and Vincent 1954) has reported on the use of 40% HF to etch an intergrowth of two cubic oxide minerals. Many of the techniques outlined in standard works on ore microscopy are, however, of little value for the examination of the ferromagnetic oxide ores.

It is doubtful whether even with the perfected methods of measuring reflective power the relationship between this property and composition in the various series of ferromagnetic minerals would be such as to permit the composition, and hence certain magnetic properties, to be deduced from a measurement of reflective power alone. The main use of the ore microscope in mineralogical observations attendant upon studies of the magnetism of rocks will probably still be found in the examination of textures, intergrowths etc. It is therefore important that no physical or chemical change shall be brought about in the material during the preparation of the section such as might result from overheating due to a drying-out of the polishing lap etc. Phillips (in Phillips and Vincent 1954) has described crystallites of ulvöspinel in titaniferous magnetite, the formation of which he attributes to local overheating during repolishing of the specimen, and Hallimond (*op. cit.*) mentions tarnishing of chacopyrites which may arise from the high speed and dryness of the lap. Care must therefore be exercised throughout the preparation of the polished section to avoid such changes affecting the magnetic components of the rocks being studied.

2. Other methods of examination of the opaque minerals of rocks involve a separation of the minerals from the rock. Two techniques of separation are commonly employed; magnetic and gravitative settling in heavy liquids, and the two are often used in conjunction. Both involve preliminary crushing of the rock to a powder, the grain size of which is less than that of the opaque minerals in the rock. To avoid contamination by fragments of steel that might result if the hardened steel pestles and mortars commonly employed for rock crushing were used, it is advisable to carry out pulverization of the rock fragments in apparatus of a non-magnetic alloy. Basta (1953) used two horizontal discs of Cu–Be alloy under a pressure of 3–4 tons/in.^{2}.

An initial concentration of the magnetic fraction may be achieved using a weak permanent magnet. A.C. and D.C. electromagnets have both been used for further magnetic concentration and recently Nagata, Akimoto and Uyeda (1953) have published details of a thermomagnetic separator. With this apparatus the separation is made in a N_2-filled electric furnace in order to avoid oxidation of the samples. The fraction to be separated, contained in a horizontal specimen tube, is spread out over a brass plate in a layer a single grain thick. A moveable electromagnet traverses along the specimen tube attracting to its upper surface those grains which are still ferromagnetic at the furnace temperature. They are carried laterally beyond the limit of the brass plate and over a trap through which they are dropped into a container when the current through the magnet is cut off. The traverse is repeated until no more grains are pulled up by the magnet. Grains will only be so attracted if their magnetization exceeds a certain critical value specific to the equipment (2·1 e.m.u./g in Nagata's equipment) so that the temperature of separation will not be the Curie Point of the separated fraction but some temperature below this. The perfection of the separation will depend on the form of the Js–T curves for the different components in the original fraction. If $\delta Js/\delta T$ for values of T near the Curie Point is high, as in the case of ore minerals similar to magnetite in composition, good separations of ores quite similar chemically should be obtained, but where $\delta Js/\delta T$ is small as in hematite, separations will be less satisfactory. As with all methods of separation the presence of composite grains of silicate and ore will complicate the separation and it may be necessary to remove them by hand picking under a binocular microscope.

The high density ($>4{\cdot}5$) of most of the ore minerals compared with the common rock-forming silicates permits them to be separated by a liquid of such specific gravity that the silicates float in it and the ores sink. Various heavy liquids may be used e.g. methylene iodide (S.G. 3·315 at 20°c) and Clerici's solution. The latter, a concentrated solution of thallous formate–malonate has a S.G. of 4·25 at room temperature, 4·4 at 35°c, 4·65 at 50°c and 5·10 at 100°c. Its preparation has been described by Vassar (1925) and its restandardization by Hawkins (1932). It is particularly valuable for separations of the ores. Centrifuging the rock powder in the heavy liquid speeds up the separation. To obtain the best possible results it is necessary to have the grain size of the rock powder within relatively narrow limits and in any case the finest powder must be removed by sieving or washing in order that particle co-agulation may be prevented. Even with the powder grain size below the average grain size of the opaque minerals in the rock composite grains will persist and these must be removed by centrifuging the nearly pure-ore fraction in Clerici's solution of specific gravity as close to the density of the ore as is practicable. It is often necessary as a final stage to hand pick grains of ore contaminated with silicate from pure ore grains in order to obtain a really pure concentrate.

For both kinds of separation the best results are obtained if powders of uniform grain size are used and to obtain the pure ore minerals for further examination and analysis such powders should be used. But during the initial crushing minerals of different hardness values will crush to different grain sizes and the percentage of ore in a powder of any selected grain size will not usually be that of the ore in the rock. Unless all the crushed rock is separated—and this is generally impracticable—the percentage of ore obtained in the separation should not be regarded as indicative of the content of ore in the rock. The latter is better determined optically by micrometric analysis (Chayes 1949).

The separated ores are then examined by x-ray crystal diffraction methods, magnetically and chemically.

(i) Identification of phases present by x-ray powder photography. Simple inspection of the pattern of the lines on a powder photograph permits reference of an ore mineral to the cubic, rhombohedral or sulphide groups but more precise identification usually involves a determination of the dimensions of the unit cell. The accuracy attained will depend on the quality of the photography but with resolution of the high angle doublets the accuracy should exceed 0·2% and may approach 0·02% (Henry, Lipson and Wooster 1951, p. 191). Basta (1953) claimed that his determination of the cell dimension of magnetite, $a=8{\cdot}3963$ Å, was accurate to 0·0005 Å. He used CoK_α (iron filtered) radiation in a 114·6 mm diameter camera and measured the film in a Hilger measuring apparatus, deriving the cell dimension by the extrapolation method of Nelson and Riley (1945) after plotting values of the cell dimensions, calculated from the high angle lines, against the function $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta/\theta)$. He reported an improvement in the quality of the photograph after annealing the magnetite by heating to 300–400°c for a few minutes in an evacuated silica glass tube, and attributed this to recrystallization of crystals which had suffered strain and dislocation during the grinding of the materials. With determinations of this accuracy it might appear that the composition of an ore of the spinel series Fe_3O_4–Fe_2TiO_4 (cell dimension variation from 8·396 for Fe_3O_4 to 8·5 for Fe_2TiO_4) could be accurately determined from the cell dimension alone if variation of cell dimension with composition is linear (law of Végard). While this may perhaps be permissible for synthetic preparations known to be intermediate between the two end members it is not so where there is a possibility of the composition lying outside this restricted range. In view of the existence of solid solutions intermediate between $FeTiO_3$, Fe_2TiO_4 and Fe_3O_4 and possessing the spinel structure, it is doubtful whether even the composition of synthetic spinels should be predicted from their cell dimensions. The composition of natural minerals certainly should not. Ionic replacements within the lattice of the mineral will modify the cell dimensions and the same value may be obtained for ores chemically dissimilar. Basta (*op. cit.*, p. 148) reports a spinel from Magnet Cove, Arkansas which contains 10% Fe_2TiO_4 and considerable Fe_2MgO_4, $MgAl_2O_4$ and Fe_2MnO_4

to have the same cell dimensions as magnetite and comparable replacements may occur in the rhombohedral series of ores. Nevertheless, determination of the cell dimensions should never be omitted in the study of an ore mineral—the relationship between the volume of the unit cell, density, chemical composition and structure as possibly indicative of the presence or absence of defects in the structure should never be lost sight of in any mineralogical investigation.

X-ray powder photographs have been used to check the purity of separations. The amount of impurity which can be so detected depends on the difference in lattice dimensions of the minerals in the mixture. With different structures, e.g. ilmenite and magnetite as little as 2–3% impurity may be detected but if the structures are the same and the cell dimensions similar it may be impossible to detect quite appreciable amounts of impurity by the usual methods of X-ray powder photography. If an X-ray spectrometer is used rather better results may be expected.

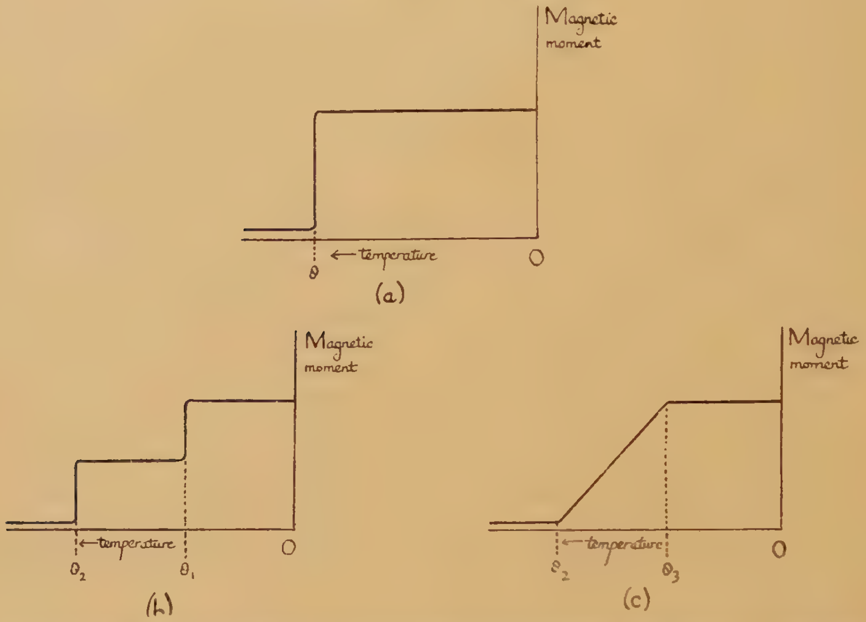
(ii) Thermomagnetic investigations such as those carried out by Chevallier and Pierre (1932), or, more recently, Chevallier, Mathieu and Vincent (1954) may indicate the degree of homogeneity of the material. A photographic record is taken of the variation in magnetic moment of each sample as a function of temperature in a constant magnetic field of about a hundred gauss. The Curie Point may be read from this curve which has the form of fig. 1 (*a*) if a single phase of uniform composition is present, of fig. 1 (*b*) if two phases are present and of fig. 1 (*c*) if the ferromagnetic material varies regularly in composition as it would do in zoned crystals. The method is not sensitive enough to be used to check the purity of separations but it enables the number of ferromagnetic minerals in a rock to be determined since the unseparated rock powder can be examined as well as the separated ores.

Another type of investigation yielding information of the number of ferromagnetic minerals in a rock is the measurement of the partial thermo-remanent magnetization acquired by a specimen subjected to the influence of a known field over a known temperature interval while cooling from *ca.* 700°C to room temperature, this cooling being in field-free space except over the chosen temperature interval. Diagrams prepared to show the intensity of partial thermo-remanent magnetization acquired on cooling in a field through different temperature ranges may show one or two temperature intervals during which the intensity of acquired partial thermo-remanent magnetization attained a local maximum (fig. 2). The number of local maxima corresponds to the number of ferromagnetic components in the rock and their approximate Curie Points may be deduced from the form of the diagram.

Purely physical measurements, e.g. of saturation magnetization, will not be described here. An account of various methods and the apparatus used has been given by Nagata (1953 a).

(iii) Chemical analysis of the ore minerals is the most certain method of composition determination. Errors in the analytical methods used and impurities in the fractions analysed are the chief sources of inaccuracy. Analyses of intergrowths of ores originating by exsolution of an earlier homogeneous phase, while having only restricted value for the correlation of magnetic properties with composition, yield valuable data on the range of composition possible in natural ore minerals, particularly the extent of possible solid solution at high temperatures. Vincent (in Phillips and Vincent 1954, p. 9) has published analytical methods suitable for the determination of the main constituents of the ores—minor constituents may be determined more rapidly by spectrographic procedures. Analyses are expressed in terms of oxides and the anion content of the oxide minerals is not determined independently. In analyses of the sulphides, sulphur is determined separately so that for these minerals both cation and anion contents are independently known and it is possible to calculate from cell dimensions, density and chemical composition the numbers of the

Fig. 1



Diagrams of possible forms for thermomagnetic curves of variation of magnetic moment against temperature determined by the method of Chevallier and Pierre (1932).

(*a*) When a single phase of uniform composition is present (θ—Curie Point).

(*b*) When two phases are present (θ_1 and θ_2—Curie Points of the two phases).

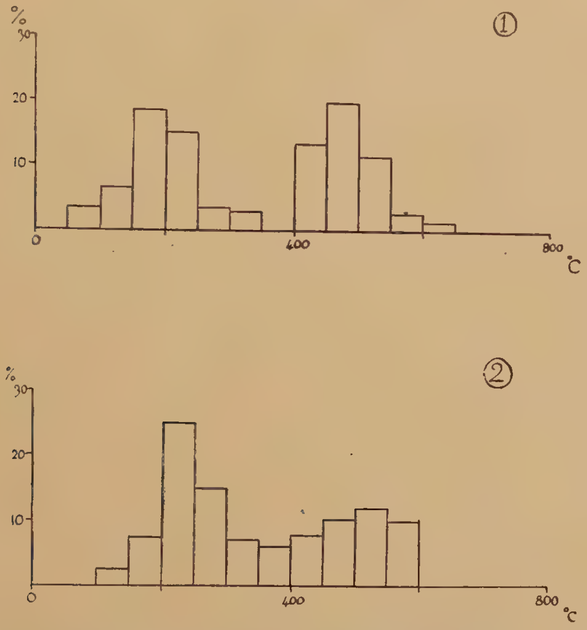
(*c*) When the ferromagnetic material varies regularly in composition (with Curie Point varying between θ_3 and θ_2).

(After Chevallier, Mathieu and Vincent 1954.)

various kinds of ion in the unit cell, and thus deduce the presence or absence of defects in the cell.

Fe^{+++}, Fe^{++} and Ti^{++++} may enter into the structure of several other common minerals in rocks, e.g. pyroxenes and olivines, so that attempts to predict the nature and content of the oxide ore minerals from the content of Fe_2O_3, FeO and TiO_2 in the rock are foredoomed to inaccuracy. For example a gabbro from Skaergaard, East Greenland containing 3·41% Fe_2O_3, 14·86% FeO and 2·59% TiO_2 is found by calculation to possess 4·87% normative magnetite and 5·02% normative ilmenite; whereas the true content of magnetite is 7·3% and of ilmenite 6·2%, the magnetite containing 42·95% Fe_2O_3, 35·68% FeO and 16·28% TiO_2 and the ilmenite 6·26% Fe_2O_3, 40·39% FeO, and 49·89% TiO_2. The contents of these oxides in the pyroxene from an adjacent rock were Fe_2O_3 0·78%, FeO 17·56%, TiO_2 1·86% pyroxene making up approximately 50% of the gabbro considered (data abstracted from Wager and Deer 1939, and Phillips and

Fig. 2



The intensity of partial thermo-remanent magnetization acquired by two specimens of Icelandic lava over different temperature intervals. The intensity in any temperature range is expressed as a percentage of the total thermo-remanent magnetization acquired by the rock on cooling from temperatures above the Curie Points of its contained ferrimagnetic minerals. The two maxima on the diagram for each of the two specimens indicate that in both cases two ferrimagnetic minerals are present. For specimen 1 the Curie Points of these two minerals are *ca.* 600–650°C and *ca.* 350°C—for specimen 2 they are *ca.* 600°C and *ca.* 300–400°C. (*After Hospers* 1953.)

Vincent 1954). The norm of a rock merely represents the chemical analysis recast in terms of a series of hypothetical mineral molecules e.g., albite $NaAlSi_3O_8$, ferrosilite $FeSiO_3$ etc.—the so-called normative minerals. In the course of the calculations all the Fe_2O_3 shown in the rock analysis is recast into magnetite and all the TiO_2 into ilmenite, excess FeO then remaining being used to form $FeSiO_3$ or Fe_2SiO_4 (dependent on the amount of SiO_2 present). The actual amount of a mineral in a rock (as opposed to the normative content of that normative mineral most similar to it in composition) is called its modal content. Since Fe_2O_3 enters other minerals as well as magnetite the normative content of magnetite (Fe_3O_4) might be expected to exceed the modal content of the spinel ore mineral. Any Fe_2TiO_4 present in the latter however, will be recast as ilmenite ($FeTiO_3$), the excess FeO entering silicate molecules so that normative magnetite may be less than modal ' magnetite '. Generally the latter of these two effects exceeds the former with the result that normative magnetite is often below its modal content. TiO_2 enters other minerals as well as the ilmenite in natural rocks with the consequence that normative ilmenite may be greater than modal ilmenite. This is especially so if the spinel ore contains much Fe_2TiO_4. But natural ilmenites usually contain some Fe_2O_3 which will tend to augment the modal content of ilmenite as opposed to the normative content. Equality of modal and normative contents of magnetite or ilmenite is more likely to be due to a balance of these effects rather than any fundamental relationship between the two contents.

On the other hand if as Chevallier, Mathieu and Vincent (1954) suggest the saturation magnetization of a spinel ore mineral at 20°c is governed by the concentration of Fe_3O_4 in the material, a prediction of the saturation magnetization of a rock from its normative content of Fe_3O_4 should be in error only to the extent to which Fe^{+++} enters other minerals than magnetite. Data examined by Nagata (1953 a, p. 106–107) shows that this is generally true.

§ 3. OXIDE MINERALS OF THE SYSTEM $FeO–Fe_2O_3–TiO_2$

Magnetite (Fe_3O_4), the most important magnetic oxide in rocks frequently contains some Ti and while other elements may also be present the principal variations in Curie Point and intensity of saturation magnetization in this mineral are probably to be attributed to variations in the Ti content (Pouillard 1950, p. 210). Possible variation in the proportions of Fe^{++}, Fe^{+++} and Ti^{++++} in magnetite can be best understood by reference to the system $FeO–Fe_2O_3–TiO_2$, a system which includes other oxide minerals of interest in discussions of rock magnetism, viz. hematite αFe_2O_3, maghemite γFe_2O_3, ilmenite $FeTiO_3$ and ulvöspinel Fe_2TiO_4. Also present in this system but not as yet considered important in rock magnetism studies are rutile TiO_2 (with its heteromorphs anatase and brookite), pseudobrookite Fe_2TiO_5 and an iron titanate $Fe_4Ti_3O_{12}$

(Pouillard 1950, p. 192). FeO has been reported from iron-rich volcanic rocks (Brun 1924) but the mineral was not isolated and no analytical or x-ray data supporting the identification was advanced. Mason (1943, p. 103) did not accept the natural occurrence of FeO and Ramdohr (1950) makes no mention of iozite (as the mineral was called) in his recent text-book. The compositions of these minerals are plotted in fig. 27; the properties of the more important are summarized below.

(*a*) *Magnetite* (Fe_3O_4 or $Fe^{++}\ Fe_2{}^{+++}O_4$) is cubic, commonly occurring as octahedrons or dodecahedrons. It is a member of the spinel group with cell dimensions :—

$a=8{\cdot}396\pm0{\cdot}0005$ Å	for natural magnetite from Bisperg, Sweden (Basta 1953, p. 55).
$a=8{\cdot}394\pm0{\cdot}0005$ Å	for magnetite produced in the laboratory (Tombs and Rooksby 1951, p. 475, Abrahams and Calboun 1953, p. 105).

The structure of this group is well-known, the unit cell containing 32 oxygen ions and 24 cations, 8 in 4-fold co-ordination (the f positions) and 16 in 6-fold co-ordination (the c positions). Perpendicular to a triad axis layers of oxygen ions alternate with layers of cations. Cation layers in which all the cations are in 6-fold co-ordination alternate with others in which the cations are distributed among f and c positions in the proportions 2 f to 1 c (fig. 3). Two types of spinel, normal and inverse, are known differing in their distribution of cations among the f and c positions. Writing the general formula $X_8\ Y_{16}\ O_{32}$, where X is Fe^{++}, Mg^{++}, Zn^{++} or Mn^{++} and Y Fe^{+++}, Al^{+++}, Cr^{+++} etc., the two distributions are :—

Normal 8 X in 8 f : 16 Y in 16 c.
Inverse 8 Y in 8 f : 8 X+8 Y in 16 c.

Magnetite is of the inverse type as may be indicated by writing its formula $Fe^{+++}\ (Fe^{++}\ Fe^{+++})\ O_4$. Neutron diffraction studies (Shull, Wollan and Koehler 1951) have indicated that the magnetic moments of the cations in the f and c positions are antiparallel. Magnetite is thus a typical ferri-magnetic. Nagata (1953 a, p. 30) quotes the magnetic properties of magnetite to be : Curie Point 578°C, saturation magnetization at room temperature 92–93 e.m.u./g. The direction of easiest magnetization is [111] (Bickford 1949) and the anisotropy energy of the order of 10^5 erg/cm^3 (Nagata 1953 a, p. 30). Magnetite melts at 1591°±5°C under a small but unknown pressure of oxygen, an increase in oxygen pressure with consequent increase in the proportion of oxygen in the magnetite resulting in a decrease in the temperature of melting (Greig *et al.* 1935). On cooling below 0°C the structure suffers deformation to a rhombohedral form at approximately −160°C, this form having cell parameters $a_R=5{\cdot}938\pm0{\cdot}001$ Å, $\alpha 59°\ 50'$ at −178°C (Tombs and Rooksby 1951, Rooksby and Willis 1953). Magnetite is opaque to transmitted light except in very thin flakes such as may form inclusions in micas (Ramdohr 1950, p. 659). In reflected light its reflective power is moderate (21%) and

Fig. 3

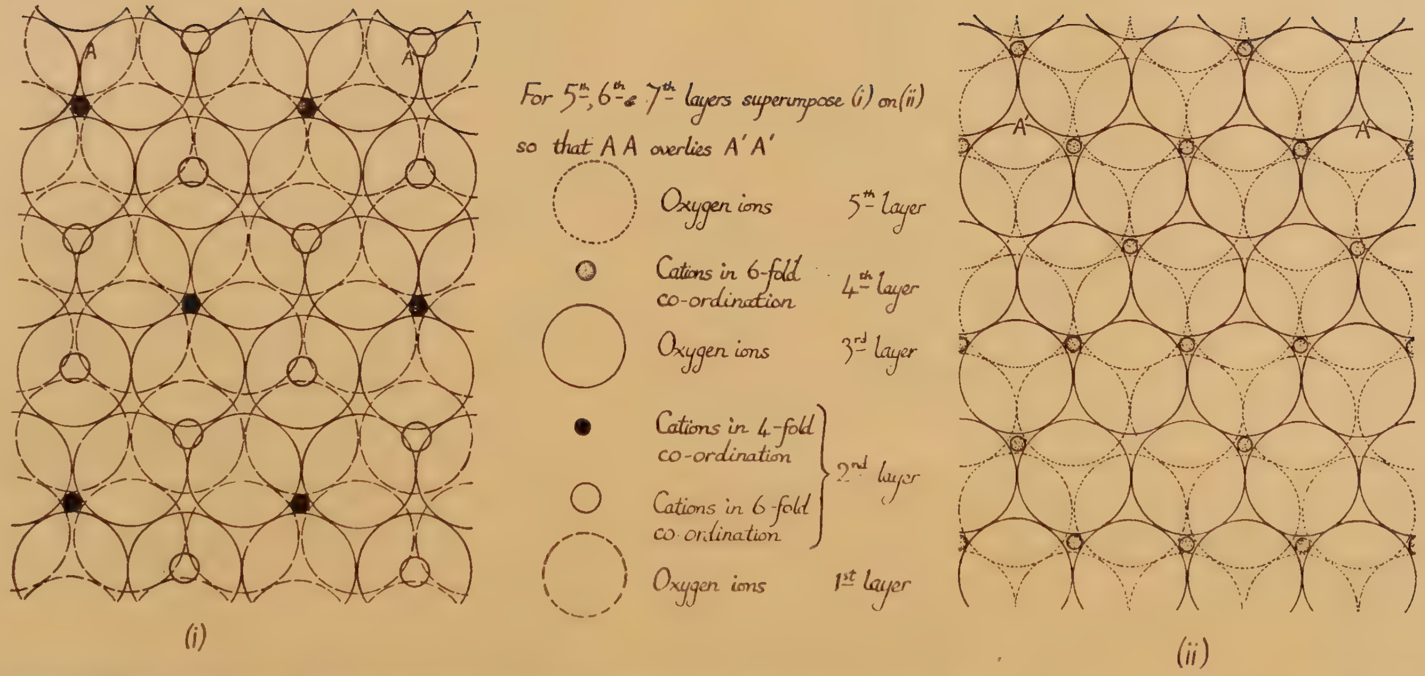

A
A'
For 5th, 6th & 7th layers superimpose (i) on (ii)
so that A A overlies A' A'
Oxygen ions 5th layer
Cations in 6-fold co-ordination 4th layer
Oxygen ions 3rd layer
Cations in 4-fold co-ordination
Cations in 6-fold co-ordination
2nd layer
Oxygen ions 1st layer
A
A'
(i)
(ii)

Diagram of the structure of the spinel group of ore minerals projected along a triad axis. Layers of oxygen ions perpendicular to the axis alternate with layers of cations: (i) and (ii) represent successive ‘ sandwiches ’ of oxygen layers with an intervening cation layer and, fitted (ii) over (i), illustrate five successive layers in the structure, the upper oxygen layer of (i) being the lower oxygen layer of (ii). Successive cation layers are dissimilar, those in which all the cations are in 6-fold co-ordination alternating with those in which two-thirds are in 4-fold and one-third in 6-fold co-ordination.

it appears grey sometimes with a light brownish tinge. Although Ramdohr (*op. cit.*, p. 658) considers that a high unexsolved Ti content may give a brownish-red tinge to the grey and Mn enhances the grey he also states that the colour tone may vary without obvious relationship to the chemistry. Magnetite is often isotropic although occasionally distinctly anisotropic, e.g., the magnetite from Kirunavaara, Sweden often used as a standard magnetite. Natural magnetites are not attacked by the normal etch reagents of Short (1948) but may slowly turn brown under attack by concentrated HCl. 40% hydrofluoric acid will etch polished sections rapidly and has been used to disclose intergrowths between magnetite and other closely related spinels (Phillips and Vincent 1954, p. 3). The density of pure Fe_3O_4 calculated from the cell dimensions determined on artificial magnetite is 5·20 though the density of natural crystals is usually slightly below this (compare Palache, Berman and Frondel 1944, p. 699).

(*b*) *Maghemite* (γFe_2O_3) is also cubic with cell dimensions $a=8{\cdot}322$ Å (Hägg 1935). It has an inverse spinel structure but compared with magnetite exhibits a lattice defect, 1 in 9 of the iron ions being absent. Verwey (1935) has shown that these ions are probably omitted from 6-fold co-ordination positions (c positions) and Haul and Schoon (1939) observed additional lines on the X-ray powder photograph probably to be interpreted as indicating a regular arrangement of the vacant positions in the lattice. Some of the iron ions must be in 4-fold co-ordinated positions in contrast to their occurrence exclusively in 6-fold co-ordinated positions in αFe_2O_3. Maghemite is metastable and, on heating, inverts to αFe_2O_3, the inversion probably being monotropic (Mason 1943, p. 108). It is assisted by pressure and accompanied by the evolution of heat suggesting that γFe_2O_3 is the high temperature form of Fe_2O_3. The inversion temperature has been variously quoted from 200 to 700°C and seems to depend on the previous history of the sample. The structure is stabilized by the entry of foreign ions e.g., Na and by a method of extrapolation from determined Curie Points of Na-bearing solid solutions Michel and Chaudron (1935) determined the Curie Point of γFe_2O_3 as 675°C. Maghemite is ferrimagnetic the saturation magnetization at room temperature being 83·5 e.m.u./g. It may be synthesized by dehydration of lepidocrocite (FeO(OH)) or by the low temperature oxidation of magnetite, a continuous process resulting in a continuous decrease in the cell dimensions and density (Hägg 1935). In transmitted light maghemite is brown to yellow in colour, isotropic and of refractive index 2·52–2·74 (Sosman and Posjnak 1925). By reflected light it appears white or grey-blue with strong reflective power (Ramdohr 1950). Under oil the colour is blue-grey similar to dry-polished magnetite. The theoretical density is 4·88 but the observed density of natural maghemites may be as low as 4·4.

(*c*) *Hematite* (αFe_2O_3) is rhombohedral with cell dimension $a_R=5{\cdot}4271$ Å, $\alpha 55°\ 15{\cdot}8'$ for a rhombohedral unit cell or for the hexagonal one $a_H=5{\cdot}0345$ Å, $c_H=13{\cdot}749$ Å, $c/a=2{\cdot}7311$ at 20°C (Willis and Rooksby

1952, p. 953). The lattice is made up of layers of oxygen ions and layers of cations in 6-fold co-ordination parallel to the triad axis (fig. 4). The oxygen ions in the anion layers are arranged in a slightly distorted hexagonal packing the 0–0 distance being 2·90 Å—cf. 0–0 distance in magnetite

Fig. 4

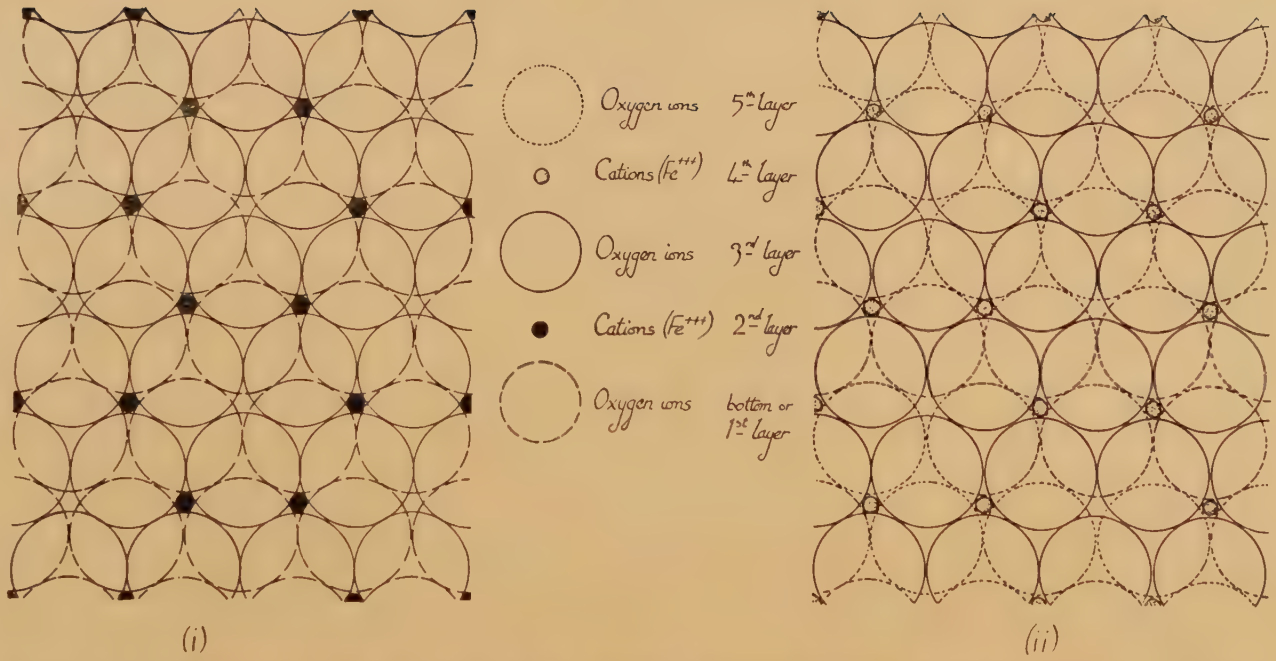

Oxygen ions 5th layer
Cations (Fe^{+++}) 4th layer
Oxygen ions 3rd layer
Cations (Fe^{+++}) 2nd layer
Oxygen ions bottom or 1st layer
(i)
(ii)

Diagram of the structure of the rhombohedral ore mineral, hematite, projected along the triad axis. Layers of oxygen ions perpendicular to this axis alternate with layers of cations: (i) and (ii) represent successive 'sandwiches' of oxygen layers with an intervening cation layer and, fitted (ii) over (i) represent five successive layers of the structure, the upper oxygen layer of (i) being the lower oxygen layer of (ii). Successive cation layers contain equal numbers of ions all in 6-fold co-ordination, thus differing from the spinel structure (fig. 3) where two-thirds of the cations in alternate layers are in 4-fold co-ordination. In hematite the oxygens of the fifth layer (third oxygen layer—top oxygen layer of 'sandwich' (ii)) are directly above those in the first layer—compare the spinel structure where this is not so.

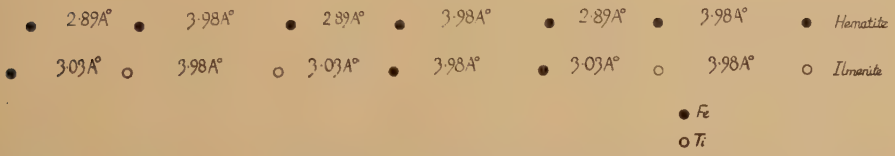
2·97 Å. In the cation layers half the iron ions are 0·29 Å above the medial plane of the layer, half are below by the same amount. By some authorities (Chevallier and Mathieu 1943, Roquet 1947) hematite is regarded as a ferromagnetic with a Curie Point 675°c and $J_s \simeq 0{\cdot}5$ e.m.u./g, $H_c \simeq 7600$ oe. Chevallier (1951) attributes its essential magnetic properties to a paramagnetism varying with temperature according to the law of K. Endo $\chi\,(T+3727)=0{\cdot}085$, χ 20°c$=20{\cdot}10^{-6}$, superimposed on a variable ferromagnetism which disappears at 675°c. Single crystals of αFe_2O_3 are reported to be paramagnetic along the triad axis but isotropic and ferromagnetic in the plane normal to this axis. Pulverization experiments suggest that the ferromagnetism only becomes evident in the plane perpendicular to the triad axis if the grain dimensions in this plane are sufficiently large and crystals of mean diameter 1 μ are reported by Chevallier to be pure paramagnetic. Other authorities believe hematite is paramagnetic above 675°c and antiferromagnetic below this temperature. Abnormality of thermal expansion (Chaudron and Forestier 1924) and an anomaly on the specific heat-temperature curve (Roth and Bertram 1929) at 675°c indicate a second order change which Néel has suggested involves a transition from a paramagnetic state above this temperature to an antiferromagnetic one below. On cooling through 675°c the structure of αFe_2O_3 undergoes a deformation involving a relative expansion along the triad axis c/a rising from 2·7223 to 2·7311 (Willis and Rooksby 1952, p. 953). This relative expansion along the triad axis is analogous to the similar effect observed in FeO and Fe_3O_4 on transition to an antiferromagnetic state. According to the views of Néel (1949) the magnetic moments of the cations in any given sheet are all parallel but antiparallel with respect to the moments in the neighbouring cation sheets. He attributes the weak ferromagnetism of natural hematite to the presence of a trace (of the order of 1%) of a rhombohedral variety of Fe_3O_4 (δ magnetite) interleaved into the hematite structure perpendicular to the triad axis. At interfaces between the two structures a layer of oxygen ions is shared the 0–0 distance being intermediate between 2·90 and 2·97 Å. The presence of 1% Fe_3O_4 in Fe_2O_3 should be disclosed by chemical analysis and where hematites contain 0·3% FeO (corresponding to *ca.* 1% Fe_3O_4) this interpretation seems generally acceptable. But Guillaud (1951 b) found ferromagnetic characters in exceptionally pure Fe_2O_3 and Chevallier (1951) states that the spontaneous magnetization is present even if the composition is strictly Fe_2O_3, provided that the individual crystals are not too small. The similarity of structure between Fe_3O_4 and γFe_2O_3 opens the question whether the latter could be deformed to a rhombohedral state while retaining its magnetic structure (6/16 of the Fe ions on one magnetic sub-lattice, 10/16 on a second) with some cations in 4-fold co-ordination. Interleaving of such 'deformed γFe_2O_3' into the hematite structure perpendicular to the triad axis could produce a weak ferromagnetism in the same way as Néel's δ magnetite but would leave the chemical constitution of the oxide strictly Fe_2O_3. The disappearance of the ferromagnetism on pulverizing grains to mean dimensions below 10 μ (Chevallier 1951) would then be interpreted as a further deformation of the γFe_2O_3 to αFe_2O_3 involving a migration of certain cations from 4-fold co-ordinated positions to 6-fold co-ordinated positions under the stresses set up during grinding. On either hypothesis the high value of the coercive force may be attributed to the extreme fine-grain of the ferromagnetic particles (Néel 1949).

Abundant very fine lamellae orientated perpendicular to the triad axis, just visible under very high magnification and favourable conditions of examination in reflected light, have been reported in a number of hematites many of which are theoretically pure Fe_2O_3 (see Ramdohr 1950, p. 693). Ramdohr favoured an origin by microtwinning rather than exsolution for them but they are too small for certain identification and might be related to interleaving of the hematite with structures such as δ magnetite or 'deformed γFe_2O_3'. More recently Néel (1953) has suggested that the properties of hematite result from the presence of a fundamental antiferromagnetism superimposed on a weak parasitic ferromagnetism, one hundred to one thousand times smaller than that of ordinary ferromagnetics. The simplest interpretation of the parasitic ferromagnetism is to suppose that the antiferromagnetism is not perfect, the two magnetic sub-lattices of the hematite not being quite identical. Such dissymmetry could be due to slight compositional irregularities as discussed earlier, or alternatively to the presence of a kind of elementary domain within which the sub-lattices were not equivalent either for geometrical reasons or because of local composition fluctuations (though the total composition remains Fe_2O_3), so that each domain possessed a resulting spontaneous magnetization, the compensation between domains then not being perfect.

On heating in air hematite dissociates to Fe_3O_4 at *ca.* 1390° (Mason 1943, p. 118)—its true melting point under sufficient pressure of oxygen to prevent dissociation probably lies between 1700 and 1800°C. In thin sections hematite is blood red in transmitted light and its refractive indices for Na yellow light are quoted by Ramdohr (1950) as ω 3·22, ϵ 2·94. In reflected light it is a bright white with grey undertone, the latter being more apparent when the specimen is viewed under oil. It is anisotropic and shows very weak reflection pleochroism in air from white (o ray) to a very pale grey-blue (e ray) but under oil this pleochroism is more marked. Its reflective power is moderate Ramdohr (1950) quoting the following values: using a photometer ocular, 21–26% in air, 10·5–15·5% in oil; using a photocell R_o 24·4–27·8, R_e 21·7–24·9 in air. When seen inner reflections are deep red in air but their number depends very much on the perfection of polishing and grain development. The normal etch reagents have little effect on hematite but Osborne (1928, p. 450) obtained good structure etching using cold concentrated HCl for 1–2 hours. Cold concentrated HF is said to etch hematite in 1–2 minutes though Osborne found HF to have no effect. The theoretical density of hematite is 5·256; crystals give similar values but poorly crystalline or earthy specimens may give values appreciably below this.

(*d*) *Ilmenite* ($FeTiO_3$) is also rhombohedral with cell dimensions $a=5{\cdot}523$ Å, α 54° 51′ for a rhombohedral unit cell or for a hexagonal one, $a_H=5{\cdot}079$ Å, $c_H=14{\cdot}135$ Å in natural ilmenite (A.S.T.M. index card 3–0781, 1950). Ilmenite synthesized in the laboratory has $a=5{\cdot}48$ Å, α 53° 46′ (Michel and Pouillard 1948). By measuring the x-ray absorption edge of Ti in ilmenite and comparing it with that in Ti compounds of known valency Hámos and Stscherbina (1933) concluded that the iron was divalent and the titanium tetravalent in this mineral. The structure is similar to that of hematite with some distortion in the oxygen layers so that the minimum 0–0 distance is 2·40 Å (Posnjak and Barth 1934, p. 273) and the separation of cations along the triad axis is slightly different. In hematite the iron ions are alternately $3{\cdot}98\pm0{\cdot}1$ and $2{\cdot}89\pm0{\cdot}1$ Å apart. In ilmenite pairs of titanium ions alternate with pairs of iron ions along this axis, the distance between a pair of titanium ions or a pair of iron ions again being $3{\cdot}98\pm0{\cdot}1$ Å but the distance between adjacent ion and titanium ions is $3{\cdot}03\pm0{\cdot}1$ Å (fig. 5). This paired distribution of cations along the triad axis involves an uneven distribution of iron and titanium ions in successive cation layers perpendicular to the triad axis; layers in which all the cations are iron alternating with layers in which they are all titanium. Ilmenite is reported to be antiferromagnetic by Nagata (1953 a, p. 36) but Akimoto (1954, pp. 4–5) reports a room temperature intensity of saturation magnetization of 0·2 e.m.u./g and a Curie Point of 100–150°C for an ilmenite from Japan with cell dimensions $a_R=5{\cdot}540$ Å, α 54° 44′. Antiferromagnetism of the ilmenite structure could be due to the antiparallel orientation of the magnetic moments of the ions in successive iron layers although within one layer all were parallel or to an antiparallel orientation of the magnetic moments of the iron ions in each iron layer (fig. 6). In the latter case structurally equivalent iron ions would have their moments parallel although in different layers. There is no evidence yet which of these magnetic structures is the correct one. Akimoto (1954, p. 13) attributes the feeble ferromagnetic property of the ilmenite he examined to a parasitic ferromagnetism arising from the local imperfect compensation of two sub-lattices coupled antiferromagnetically along the lines of Néel's suggestion for hematite (Néel 1953).

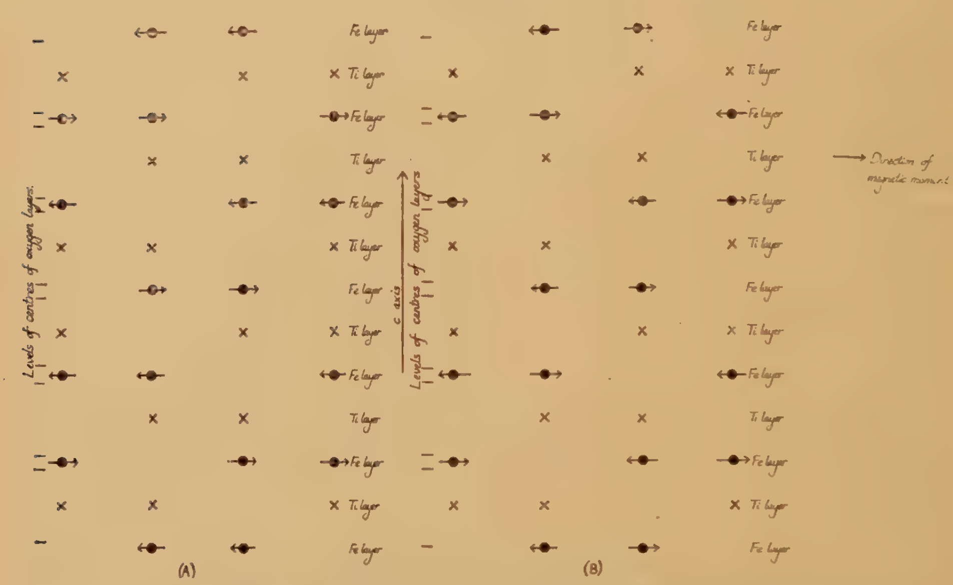
Fig. 5



The distribution of cations along the triad axis in hematite and ilmenite. Pairs of titanium ions alternate with pairs of iron ions in the latter, the distance between adjacent iron and titanium atoms being 3·03 Å.

Ilmenite melts at 1470°C. Except in extremely thin flakes it is opaque to transmitted light and in reflected light is grey white with a light brownish tinge or, under oil, distinctly brownish grey (Ramdohr 1950, p. 699). It is anisotropic with reflection pleochroism very weak in air but quite marked in oil, from white with a brownish tinge (o ray) to distinct brown (e ray). Reflective power is only moderate (18% in air, 6·5–7·5% in oil using the photometer ocular: $R_o = 21\cdot0$, $R_e = 18\cdot0$ in air using the photocell). Inner reflections are rarely seen. The normal etching reagents have no effect but concentrated HF or HF and H_2SO_4 give appreciable corrosion. The theoretical density is 4·79 but observed densities are usually slightly below this.

Fig. 6



Alternative possibilities for the magnetic structure of ilmenite—the structure is viewed perpendicular to the triad axis and is illustrated diagrammatically, only the centres of the cations being strictly positioned. The unit of magnetic structure in A, in which all the magnetic moments of one iron layer are parallel, is twice as large as that in B where antiparallel orientation of the magnetic moments occurs in each iron layer.

(*e*) *Ulvöspinel* (Fe_2TiO_4) is cubic of inverse spinel structure analogous to magnetite with 2Fe^{+++} replaced by Fe^{++}Ti^{++++}. In all but one of the reported natural occurrences it is a component of a fine intergrowth with magnetite and pure Fe_2TiO_4 has not yet been isolated and analysed from a natural deposit. Artificial Fe_2TiO_4 was first prepared by Barth and Posnjak (1932) who quoted the cell dimension as 8·5±0·1 Å. Later determinations include 8·49±0·010 Å (Ernst 1943) and 8·534 Å (Pouillard 1950, p. 195). Nagata (1953 a, p. 37) states that Fe_2TiO_4 is paramagnetic. The melting point of ulvöspinel is 1470°C (Grieve and White 1939). By reflected light ulvöspinel appears darker brown than the magnetite with which it is usually associated though colour is not apparently a safe criterion for the recognition of this mineral (Ramdohr 1953, p. 681). In the fine intergrowths the distinction between ulvöspinel and ilmenite may be particularly difficult if the mineral in question is too fine-grained to show possible anisotropy. In such cases it is useful to recall that lamellae of ulvöspinel in magnetite are often orientated parallel to {100} (the cube faces) of the latter while ilmenite lamellae are usually parallel to {111}—the octahedral faces. Where original ulvöspinel has undergone oxidation to ilmenite the latter mineral extinguishes obliquely to the length of the lamella (Ramdohr, *op. cit.*, p. 682). The calculated density of Fe_2TiO_4 is 4·835 using Barth and Posnjak's value for the cell dimension, or 4·777 if Pouillard's figure is taken.

Of the other definite compounds occurring in this system a ferric titanate $Fe_4Ti_3O_{12}$ with a tetragonal structure, $a = 9{\cdot}30$ Å, $c = 9{\cdot}50$ Å, synthesized by Pouillard and Michel (1949) is weakly magnetic with a Curie Point 240°c. The three forms of TiO_2 rutile (tetragonal), anatase (tetragonal), brookite (orthorhombic) are found naturally but make no significant contribution to the magnetic properties of rocks. Pseudo-brookite (Fe_2TiO_5) is rather rare.

Oxide minerals occurring naturally in rocks rarely conform to the pure compositions, Fe_3O_4, Fe_2O_3 etc. Usually they are intermediate in their chemistry and their properties are best discussed in terms of solid solution series, viz. the Fe_3O_4–Fe_2TiO_4 series, the Fe_2O_3–$FeTiO_3$ series, the Fe_3O_4–$FeTiO_3$ series and the Fe_3O_4–Fe_2O_3 series.

The Fe_3O_4–Fe_2TiO_4 *Series*

Solid solution is believed to be complete between the two spinel end-members of this series and the investigations of Pouillard (1950) and Kawai, Kume and Sasajima (1954) show that it is certainly very extensive. Pouillard synthesized several spinels with cell dimensions intermediate between pure Fe_3O_4 and Fe_2TiO_4 and has shown that the Curie Point of magnetite is considerably affected by the ionic replacement $2Fe^{+++}$–$Fe^{++}Ti^{+++}$. His results are reproduced in table 1. The

Table 1. Variation of Cell Dimensions and Curie Point in Series Fe_2TiO_4–Fe_3O_4

	1	2	3	4	5	6	7	8
Cell dimension *a* in Å	8·413	8·420	8·428	8·43	8·44	8·46	8·46	8·534
Curie Point	575°c	524°c	485	475	468	230	215	—
mol. % $TiFe_2O_4$	0	8	10	18	25	42	42	100

Data from Pouillard (1950).

spinels whose properties are given in cols. 2, 3, 4 and 5 were synthesized by heating mixtures of TiO_2 and Fe_3O_4 *in vacuo* for one hour at 900°C (Pouillard 1950, p. 203)—those to which cols. 6 and 7 refer were produced by reducing mixtures of TiO_2 and Fe_2O_3 with H_2 for two hours at 450°C and subsequently homogenized by holding for one hour at about 900°C. In each case other phases were formed as well and Pouillard acknowledges that the compositions of these solid solutions are not known with certainty. The evaluation of the molecular percentages in the last line of the table was made by application of the law of Végard (proportionality of crystal parameters to molecular composition), and assumes that the synthesized spinels are truly intermediate between the two end members. This is not necessarily so—they may have compositions lying on the Fe_2O_3–$FeTiO_3$ side of the direct join. Chevallier and Girard (1950, p. 577) interpreted Pouillard's figures as a direct relationship between composition and Curie Point for the series $x Fe_3O_4 . (1-x) Fe_2TiO_4$ expressed by the law $\theta°K=850x$ where $\theta°K$ is the Curie Point. Combined with the law of Végard this relationship should lead to a direct variation of Curie Point with cell dimension in this series as shown by AB and AB′ of fig. 7. In drawing these lines the more recent value for the cell dimension of magnetite $a=8{\cdot}396$ Å has been used in preference to Pouillard's value $a=8{\cdot}413$ Å (represented by A′ in the figure). B records the cell dimension of Fe_2TiO_4 according to Barth and Posnjak $a=8{\cdot}5$ Å, B′ Pouillard's value $a=8{\cdot}534$ Å. The Curie Points of all Pouillard's preparations are higher than would be expected for spinels of the observed cell dimensions lying on the $Fe_3O_4 . Fe_2TiO_4$ join, if the line of variation corresponding to the more recently determined values of cell dimensions (line AB′) is used though a better fit is obtained if Pouillard's value for the cell dimension of magnetite is used (line A′B′). This may be an indication that his spinels are not strictly intermediate between Fe_3O_4 and Fe_2TiO_4 or that the relationship advanced by Chevallier and Girard is not always operative. Later in their paper these authors suggested that the relationship of Curie Point to composition in the cubic ferromagnetic oxides can be expressed by

$$\theta°K=1245s \qquad \text{where } s=\frac{\text{wt.\% } Fe_2O_3}{\text{wt.\% } Fe_2O_3+FeO} \qquad \text{(curve ABC of fig. 9)}$$

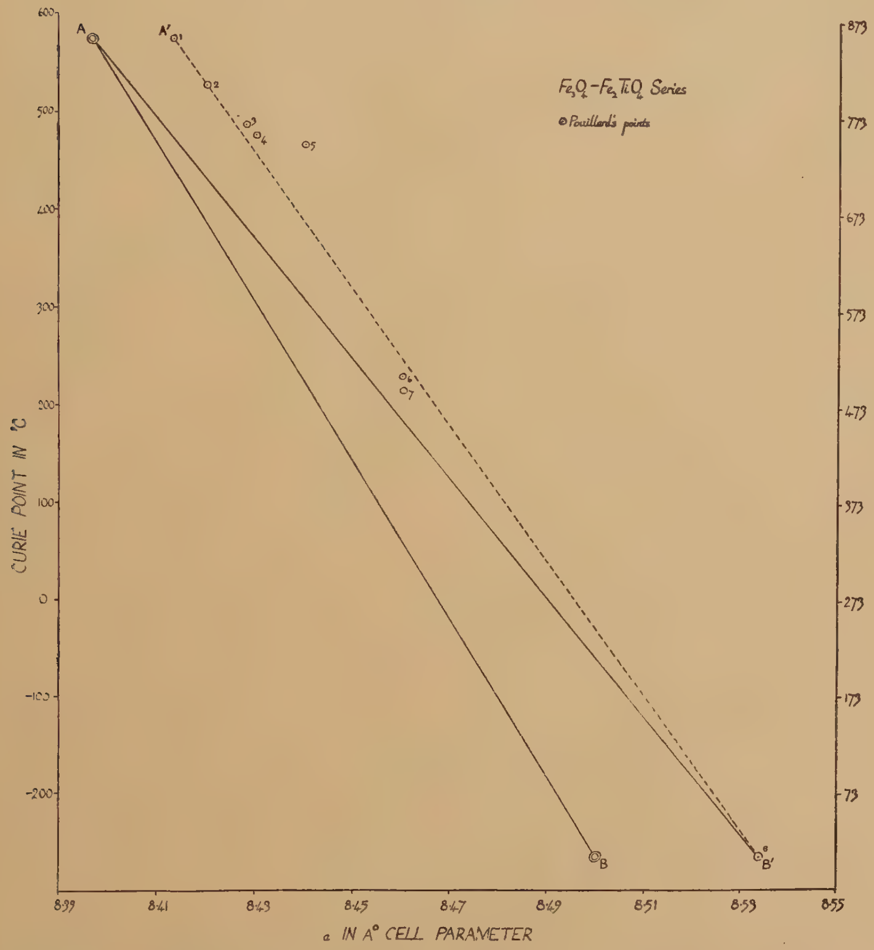
with which some of Pouillard's values accord better. Data presented by Akimoto (1954) suggests that the specific intensity of saturation magnetization may decrease with increasing content of Fe_2TiO_4 in this series. Uniform replacement of $2Fe^{+++}$ by Fe^{++} and Ti^{++++} throughout the magnetite structure (in both f and c positions) would not be expected to result in such a decrease which is much more probable if either of two possibilities occur :—

(1) Only Fe^{+++} in the c positions is replaced with a regular distribution of Fe^{++} and Ti^{++++} among the replaced positions.

(2) Fe^{+++} in the c positions is replaced by Ti^{++++} and that in the f positions by Fe^{++}.

The second suggestion accords better with the magnetic character of the end-member Fe_2TiO_4 and the relationship $\theta°K = 850x$. 75% of the titanium ions are located in the cation layers in which there are only c positions; the remainder in the mixed f c layers according to this hypothesis. Only if the titanium ions are limited to the c positions is the intensity of saturation magnetization likely to bear a direct relationship to the chemical composition and, following the theory of ferrimagnetism of

Fig. 7



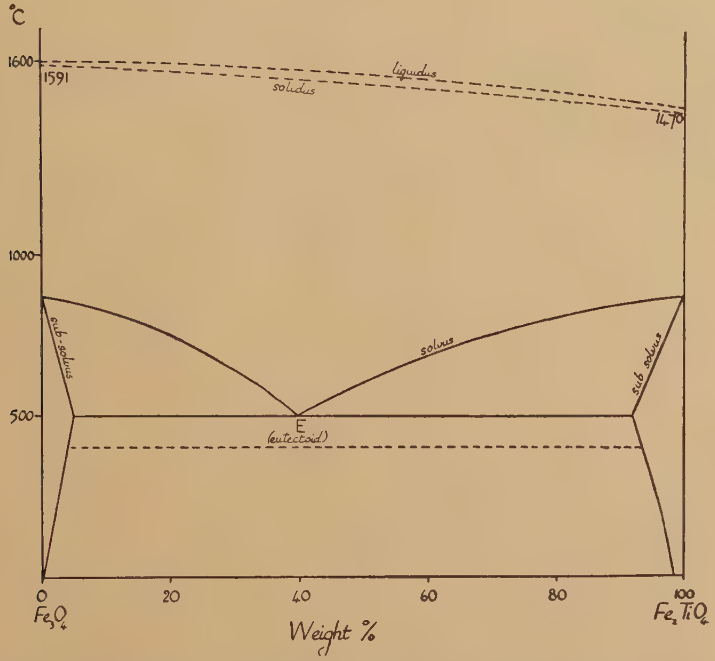
Variation of Curie Point with cell dimension in the series Fe_3O_4–Fe_2TiO_4. Magnetite is represented by A (using Basta's (1953) figure for the cell dimension) or A′ (using Pouillard's (1950) value). Fe_2TiO_4 is represented by B (using Barth and Posnjak's (1932) figure for the cell dimension) or B′ (using Pouillard's (1950) value).

The points plotted refer to Pouillard's artificially prepared spinels.

Néel, the entry of Ti into the f positions to some slight extent might increase the intensity of saturation magnetization above the expected value for a given chemical composition. Bertaut (1952) has shown that although $MgFe_2O_4$ (a spinel similar to magnetite) has the inverse structure at low temperatures, a specimen chilled from 1200°c shows a marked degree of disorder of the cations from their theoretical distribution, there being only 39% of the Fe^{+++} ions in the f positions instead of 50% as an ideal inverse distribution requires. This may explain why the observed value of the number of Bohr magnetons per mol. of this ferrite exceeds the theoretical value (Nagata 1953 a, p. 28). Any similar departure from the ideal inverse structure for pure Fe_3O_4 or intermediates between Fe_3O_4 and Fe_2TiO_4 would tend to increase the specific intensity of saturation magnetization without change of composition. If the relationships between saturation magnetization, composition and Curie Point which are found in the ferromagnetic alloys may be applied to the oxides (compare Nagata 1953 a, p. 10) departure from the ideal inverse structure might likewise lead to an elevation of the Curie Point. In view of the temperatures at which Pouillard synthesized his spinels some degree of disorder in the cation distribution could be one explanation of the unexpectedly high Curie Points he reported. Structural evidence on the detailed distribution of the cations in the Fe_3O_4–Fe_2TiO_4 series of spinels is at present lacking and would not be easily obtained in view of the similarity of x-ray scattering power of the ions involved. But it should not be expected that an absolute correlation of Curie Point or saturation magnetization with chemical composition will be found in the Fe_3O_4–Fe_2TiO_4 series and exceptions to the Chevallier–Girard relationship could well occur among the spinels of this series found in volcanic lavas. Kawai, Kume and Sasajima (1954) have extended the range of synthesized spinels to 80% Fe_2TiO_4 at which composition the Curie Point is recorded as −45°c. They do not record their method of synthesis or the way in which the composition of the synthesized product was determined. It is clear however, that at the temperatures of synthesis solid solution extends over much, if not all, of the Fe_3O_4–Fe_2TiO_4 range.

At lower temperatures solid solution is much more restricted and intermediate compositions exsolve on cooling into two separate spinel phases. The exsolved component usually forms lamellae parallel to the cube faces {100} of the host crystal as described by Ramdohr (1953) and in most cases it is the more titaniferous of the two spinels (Mogensen 1946, Phillips and Vincent 1954). The sub-solidus relationships in this system are still rather obscure. Phillips (in Phillips and Vincent, *op. cit.*) has suggested they could be explained if the phase diagram had the form shown in fig. 8. The evidence for the eutectoid point depends on the interpretation of a ' cloth-texture ' intergrowth and the identification of small crystallites in host magnetite as ulvöspinel of primary origin. Kawai, Kume and Sasajima (1954) present a different diagram reproduced in modified form as fig. 9. These authors kept magnetites at various temperatures and determined the phases of the crystals in equilibrium at each temperature by measuring Curie Points and referring them to the linear correlation with molecular percentage composition mentioned earlier in this section. There may therefore be some slight error in the position of their solvus curve but its form should be substantially correct. A spinel solid solution such as X would be homogeneous at temperatures greater than *t* but at this temperature lamellae of composition Y would separate out if cooling is sufficiently slow for equilibrium to be established and maintained. The separation of the lamellae causes the composition of the host crystal to change along X X′ X″ while the composition of the lamellae changes along Y Y′ Y″. Chilling from any temperature would prevent further exsolution and preserve the intergrowth existing at that temperature. Thus the original homogeneous solid solution X could be represented by an intergrowth of X′ and Y′ if chilled from a temperature *t*′ or X″ and Y″ if the cooling was rapid from *t*″. Since in the X′Y′ intergrowth the proportion of X′ to Y′ would be Y′z of X′ to zX′ of Y′ and in the X″Y″ intergrowth Y″z′ of X″ and z′X″ of Y″ the proportion of the second (in this case, more titaniferous) component increases with continued

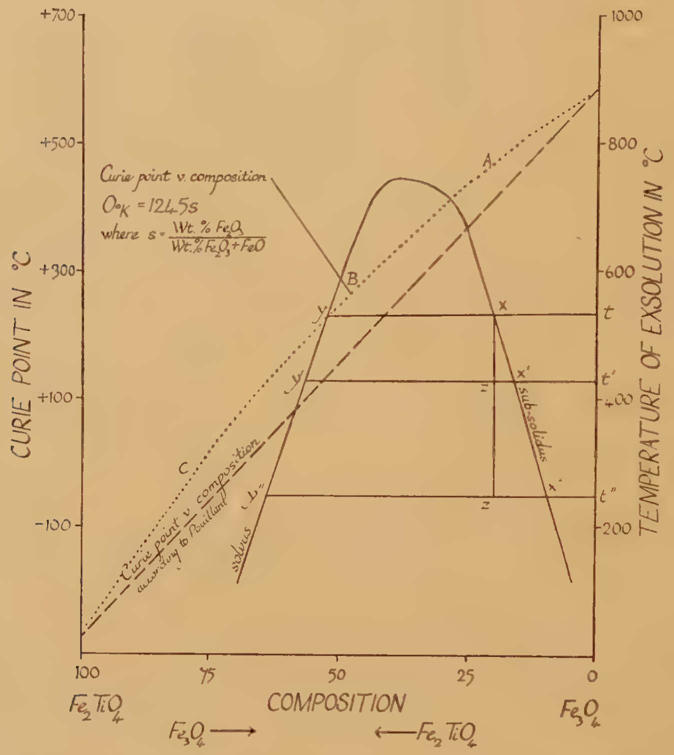
Fig. 8



Sub-solidus relationships in the system Fe_3O_4–Fe_2TiO_4 after Phillips (Phillips and Vincent 1954). The distinctive feature of this interpretation is the eutectoid E on the solvus curve, with the implication that compositional change in one of the two components of an exsolving intergrowth will not be continuous with falling temperature under certain conditions.

exsolution. If present in only a small amount the second component will have little effect on the form of the thermomagnetic curve and the Curie Point reported for such an intergrowth will be that of the more abundant component. Natural ores of the same chemical composition may therefore give different Curie Points in consequence of the differing extents to which exsolution has proceeded in them. In ores of compositions near X continued exsolution would lead to an apparent rise in Curie Point, while the reverse process, homogenization by heating of an intergrowth of two spinels, could lead to an apparent fall in Curie Point such as has been observed by Akimoto (1951 and 1954) for a number of natural ore minerals (but see also p. 171 of this paper).

Fig. 9



Sub-solidus relationships in the system Fe_3O_4 . Fe_2TiO_4 after Kawai, Kume and Sasajima (1954). These authors interpret the solvus as a smooth curve with exsolution proceeding continuously with cooling to lower temperatures. The dashed line on the diagram illustrates the linear correlation of Curie Point with composition suggested by Pouillard (1950). The dotted line (ABC) correlates Curie Point and composition according to the Chevallier–Girard relationship $\theta°K = 1245s$ where $s = \frac{\text{wt.\%}Fe_2O_3}{\text{wt.\%}Fe_2O_3 + FeO}$. For the meaning of X, X′, X″ and Y, Y′, Y″ see text.

The α Fe_2O_3–$FeTiO_3$ *Series*

At temperatures in excess of 1050° solid solution is complete between hematite (α Fe_2O_3) and ilmenite ($FeTiO_3$) as has long been known from the work of Ramdohr (1926) and Posnjak and Barth (1934). On the phase diagram the liquidus must fall from the hematite end of the series to ilmenite (fig. 10) and the solidus is probably quite close to it though zoned $FeTiO_3$-rich intermediates of this series are not uncommon. Basta (1953, p. 110) quotes figures showing a steady rise in the cell dimensions from hematite to ilmenite (table 2) for intermediate solid solutions. There is no certain evidence of any break in the variation of the cell dimensions and it would seem that the replacement $2Fe^{+++} = Fe^{++}$ and Ti^{++++} must take place continuously.

Table 2. Cell Dimensions of Hematite–Ilmenite Series of Solid Solutions (after Basta)

Composition	a_H in Å	c_H in Å	c/a
αFe_2O_3	5·029	13·73	2·730
$2Fe_2O_3.FeTiO_3$	5·0481	13·829	2·7395
$Fe_2O_3.FeTiO_3$	5·0636	13·895	2·744
$Fe_2O_3.2FeTiO_3$	5·0657	13·928	2·749
$FeTiO_3$	5·083	14·04	2·762

In reporting the occurrence of Fe_2O_3-rich ilmenites from volcanic rocks Ramdohr (1950, p. 703) mentions the increase in reflective power over that of pure ilmenite observed in intermediate members of the series but there is as yet no evidence to show whether the variation of reflective power is linear with composition.

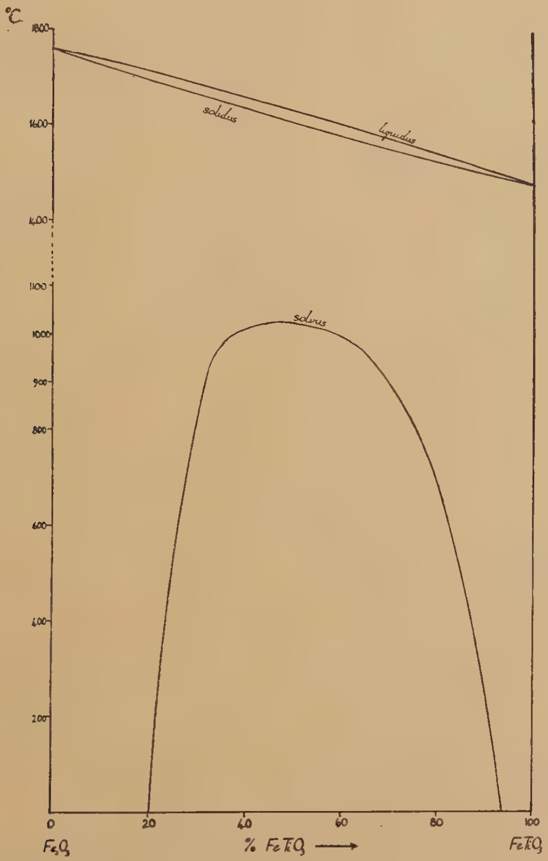
At normal temperatures solid solution is much more restricted. Edwards (1938) reports hematites with up to 10% TiO_2 (corresponding approximately to 80% hematite, 20% ilmenite in molecular proportions) and ilmenites with up to 6% Fe_2O_3. The former, called titanhematites are more grey white than pure hematite in reflected light, have lower reflective power and show strong anisotropy. They lack the deep red internal reflections of hematite and are more resistant to hydrofluoric acid whether alone or with sulphuric acid. The latter are also strongly anisotropic being pleochroic in brownish tints. They are readily etched by hydrofluoric acid or the hydrofluoric sulphuric mixture. All intermediate compositions are represented at normal temperatures by intergrowths of one mineral in the other. The inclusions form 'gashes' of variable size and shape roughly perpendicular to the triad axis of the host crystal. Within the coarser exsolution bodies small exsolution lenses of the host material may occur particularly towards the centres of the 'gashes', an indication of the progressive nature of the exsolution process. Edwards (*op. cit.*, p. 44) in describing hematite inclusions in ilmenite considers that there is abundant indication that solid diffusion has occurred during the process of exsolution. "The irregular shape of the hematite bodies, again particularly the larger ones, indicates that they have 'grown *in situ*' by absorbing exsolving hematite from the adjacent ilmenite solid solution. If they were solely the product of exsolution they would be more regular in shape and distribution. The ilmenite adjacent to the large hematite bodies is frequently free from even the minutest particles of hematite indicating that it has been drained of its content of exsolvable hematite." Such solid diffusion will involve relative movement of the cations so that the Fe^{+++} ions tend to segregate in hematite rich bodies and the Fe^{++} and Ti^{++++} in ilmenite-rich areas but the layers of oxygen anions have the same orientation in the two structures so that movement of the anions need only be relatively slight. Ramdohr (1950, p. 703) observes that the optical properties of the exsolved bodies depart appreciably from those of the pure end members and it is apparent that the ilmenite of such intergrowths always contains some Fe_2O_3 in solid solution and the hematite some $FeTiO_3$.

By holding charges of appropriate composition at 950° for 2 hours Pouillard (1950) showed that at this temperature there was a gap in the solid solution series which he deduced extended from 33% $FeTiO_3$ to 66% $FeTiO_3$. His identification of constituent phases from cell dimension determinations leaves a small margin of error but the gap can hardly be less extensive than 37% to 63% $FeTiO_3$, and hardly more so than 30% to 70% $FeTiO_3$. Basta (1953, p. 108) has shown that this gap is non-existent at 1050°C. The solvus of the phase diagram is therefore probably a smooth curve slightly asymmetrical and closing between 33 and 66% $FeTiO_3$ at a temperature between 950 and 1050°C (fig. 10). The exsolution on cooling of a homogeneous solid solution of intermediate composition takes place in a similar way to that of an intermediate in the Fe_3O_4–Fe_2TiO_4 series as described earlier. Rapid cooling inhibits exsolution and Ramdohr (1950, p. 703) has reported 'ilmenites' with contents of Fe_2O_3 exceeding 6% from volcanic tuffs and inclusions in volcanic rocks which have been subjected to rapid quenching.

Both hematite and ilmenite can take TiO_2 into solid solution. Pouillard's investigations (1950, p. 191) led him to the view that α Fe_2O_3 could only hold a restricted amount of TiO_2 and Basta (1953, p. 96) concluded that not more than 5% TiO_2 can enter at 800°C. The latter author fixed the limit of solid solution of TiO_2 in $FeTiO_3$ at 6% (by weight) at 1040°C. It appears probable that intermediates of the α Fe_2O_3–$FeTiO_3$ series can likewise hold 5–6% excess TiO_2 at these elevated temperatures but the descriptions of ilmenite–hematite–rutile intergrowths in rocks from S. Australia given by Edwards (1938, p. 54) and the observations of Ramdohr leave little doubt that the excess TiO_2 exsolves as rutile on cooling. Natural ilmenites carrying an excess of TiO_2 have been reported by Akimoto (1954, p. 4) forming phenocrysts in rapidly chilled volcanic lavas indicating that quenching from magmatic temperatures (*ca.* 1000°c) preserves these solid solutions as it does intermediates between $FeTiO_3$ and αFe_2O_3.

Intermediate solid solutions of the αFe_2O_3–$FeTiO_3$–TiO_2 series may show a weak intensity of saturation magnetization at normal temperatures comparable to that of the end members and probably to be attributed to similar causes. But occasional examples have been reported (Nagata. Akimoto and Uyeda 1953, Akimoto 1954) for which the intensity of saturation magnetization is of the order of 100 times greater, e.g., one from a volcanic pumice occurring at Haruna, Japan, with the molecular composition 26·9% Fe_2O_3, 66·4% $FeTiO_3$, 6·7% TiO_2 gave a value of 20 e.m.u./g compared with the 0·2 e.m.u./g reported for ilmenite. The Curie Point for the Haruna mineral was reported as 250°c (Akimoto 1954, p. 5),

Fig. 10



Phase relationships in the system ilmenite–hematite. Too little data is available for accurate positioning of the solvus curve but it is unlikely to differ in form from that shown here.

intermediate between that of ilmenite (100–150°c) and hematite (675°c). Data is at present insufficient for the determination of any variation of Curie Point with composition in this series (if any regular variation exists). An attempt has been made by Nagata, Akimoto and Uyeda (1953, p. 182) to explain the magnetic character of the Haruna mineral in terms of the substitution $2Fe^{+++}=Fe^{++}+Ti^{++++}$ in either of the end members ol the series. Writing the perfect antiferromagnetic arrangement for ilmenite as $(Ti_{1/2}^{++++}Fe_{1/2}^{++})(Ti_{1/2}^{++++}Fe_{1/2}^{++})O_3''$ and for hematite as

$$(Fe^{+++})(Fe^{++})O_3''$$

they suggest that the Fe^{+++}, Fe^{++} and Ti^{++++} ions of an intermediate of approximate composition $Ti_{2/3}^{++++}Fe_{2/3}^{++}Fe_{2/3}^{+++}O_3$ may be so distributed among the cation sites of the structure that a ferrimagnetic arrangement results. A distribution according well with the observed intensity of saturation magnetization is $(Ti_{1/6}^{++++}Fe_{1/6}^{++}Fe_{2/3}^{+++})(Fe_{1/2}^{++}Ti_{1/2}^{++++})O_3''$. In consequence of the segregation of cations in ilmenite into layers composed alternately of all titanium and all iron ions, the cations of one pair of brackets in the antiferromagnetic arrangement for ilmenite reproduced above do not occur in the same layer but in successive ones. In hematite the contents of one pair of brackets occur in the same cation layer. To be strictly comparable the two structural arrangements may be expressed

$$(\overrightarrow{Fe_{1/2}^{++}}\,\overleftarrow{Fe_{1/2}^{++}})(Ti_{1/2}^{++++}Ti_{1/2}^{++++})O_3'' \quad \text{and} \quad (\overrightarrow{Fe^{+++}})(\overleftarrow{Fe^{+++}})O_3''$$

where the contents of any pair of brackets lie in the same cation layer and the arrows indicate the direction of the magnetic moments. Alternatives are then possible for the arrangement of the intermediate

$$Ti_{2/3}^{++++}Fe_{2/3}^{++}Fe_{2/3}^{+++}O_3$$

viz. (i) a ' substituted ilmenite '

$$(\overrightarrow{Fe_{1/3}^{+++}}\,\overrightarrow{Fe_{1/6}^{++}}\,\overleftarrow{Fe_{1/2}^{++}})(\overrightarrow{Fe_{1/3}^{+++}}\,Ti_{1/6}^{++++}\,Ti_{1/2}^{++++})O_3''$$

and (ii) a 'substituted hematite' $(Ti_{1/6}^{++++}\,\overrightarrow{Fe_{1/6}^{++}}\,\overrightarrow{Fe_{2/3}^{+++}})(\overleftarrow{Fe_{1/2}^{++}}\,Ti_{1/2}^{++++})O_3''$. The former possibility involves selective replacement of ions occurring within the same layer which are structurally equivalent and differ only in the direction of their magnetic moment. The latter could arise through the selective replacement of Fe^{+++} in different layers but uniform replacement within any given layer. The second possibility seems much more probable and it seems likely that the quite strongly ferrimagnetic intermediates of the αFe_2O_3–$FeTiO_3$ series have the magnetic structure of a ' substituted hematite ', even when their composition is much closer to $FeTiO_3$ than Fe_2O_3, as is the case with the Haruna mineral.

Uniform replacement of structurally similar ions within individual cation layers of the ilmenite lattice would not result in the development of strong ferrimagnetism. Such ' substituted ilmenites ' should have magnetic properties not significantly different from the end member ilmenite. Akimoto (1954, p. 4) has published data (reproduced as table 3) on ilmenites from Japanese volcanic rocks showing that such ilmenites occur naturally.

In a ' substituted ilmenite ' replacement must have occurred to the same extent in each cation layer in order that the charge balance may be maintained and the layers are alternately all Fe^{++} and Fe^{+++} and all Ti^{++++} and Fe^{+++}. In a ' substituted hematite ' replacement can affect successive cation layers differently and Fe^{++}, Fe^{+++} and Ti^{++++} may occur in every cation layer, a point of distinction between these structures and ' substituted ilmenites '.

It is not certain from the data available whether any given composition can exist either as a weakly magnetic ' substituted ilmenite ' or a ferrimagnetic ' substituted hematite ' or whether ' substituted ilmenites ' only range from $FeTiO_3$ to a limiting composition with between 13 and 27 molecular $\%Fe_2O_3$, beyond which intermediate compositions have the structure of a ' substituted hematite '. Much more information is required about the variation in magnetic properties exhibited by members of the αFe_2O_3–$FeTiO_3$ series before this point can be elucidated.

' Substituted hematites ' in which replacement has affected all cation layers to the same degree, with uniform replacement of $2Fe^{+++}$ by Fe^{++} and Ti^{++++} in each layer, would of course be similar in magnetic properties to pure hematite. Only when replacement affects successive layers to different degrees is a ferrimagnetism likely to develop. Titanium-bearing hematites with magnetic characters similar to pure hematite probably have this regularly substituted structure.

The conditions determining the extent of replacement in successive layers may be connected with the origin of the intermediate rhombohedral solid solutions and, as will be discussed later, it is probably significant that the ferrimagnetic intermediates so far discovered naturally occur in volcanic rocks which suffered rapid chilling after a period of relatively slow cooling. In the laboratory they have been produced by Curnow and Parry (1954) who report that it is possible to change weakly magnetic ilmenite to a more strongly magnetic variety by heating in air at temperatures between 600°c and 800°c. They report that oxidation occurs, the ferric–ferrous ratio rising from 0·40–0·65 to 1·3, but x-ray powder photographs of oxidized magnetic ilmenites show only a few rutile lines in addition to a set indistinguishable from those obtained from the original weakly magnetic material.

The $Fe_3O_4 . Fe_2O_3$ *Series*

Only very restricted solid solution is possible between magnetite (Fe_3O_4) and αFe_2O_3 (hematite) at the temperatures of igneous rock formation according to the phase diagram for this system published by Grieg and his co-workers (1935). At 1075°c under a low, but unknown, oxygen pressure magnetite can hold $8 \pm 1\%$ excess Fe_2O_3 but the hematite can take less than $0{\cdot}5\%$ Fe_3O_4 into solid solution. At 1452 ± 5°c under an oxygen pressure of one atmosphere magnetite may carry about

Table 3. Chemical Composition, Crystallographic and Magnetic Properties of the Ferromagnetic Minerals of the Ilmenite–Hematite Series (after Akimoto 1954)

Locality	Petrological description	Composition (mol. %)			Crystal parameters		Curie Point		Intensity of saturation magnetization at room temp.
		Fe_2O_3	FeO	TiO_2	a_{rh}	α_{rh}	H °C	C °C	
Inariana, Gunma	Ilmenite ore mineral				5·540	54° 44′	100	150	0·2 e.m.u./g
Sinkamibasi, Kagosima	Phenocryst ilmenite in dacite pumice	11·8	38·8	49·4	5·539	54° 33′	110		0·2
Kaziya, Yugawara	Phenocryst ilmenite in dacite obsidian	8·3	46·0	45·7	5·523	54° 54′	100	140	0·2
Matukizawa, Asio	Phenocryst ilmenite in dacite pitchstone	6·3	42·8	50·9	5·522	54° 52′	100	150	0·2
Matukizawa, Asio	Phenocryst ferromag. min. in dacite pitchstone				5·483	55° 02′	230		21
Hatatudake Haruna	Phenocryst ferromag. min. in dacite pumice	26·9	33·2	39·9	5·480	55° 08′	250		20

Curie Point *H*—Curie Point determined during heating.
Curie Point *C*—Curie Point determined during subsequent cooling.

30% Fe_2O_3 but the content of Fe_3O_4 possible in hematite still remains less than 1%. Basta's recent observations (1953, p. 85) accord well with this earlier work. Up to 15% Fe_2O_3 in solid solution there is no noticeable change in cell dimension with increasing Fe_2O_3 content and even with 22% Fe_2O_3 in Fe_3O_4 the cell dimension of the solid solution is less than 0·01 Å below that of pure magnetite. This contrasts with the distinct fall in cell dimensions with increasing Fe_2O_3 content in the Fe_3O_4–γFe_2O_3 series and it has been claimed to be a possible method of distinction between the two types of $Fe_3O_4 . Fe_2O_3$ solid solution.

Intergrowths of hematite and magnetite have been reported from natural occurrences (Newhouse 1936, p. 19, Edwards 1949, Baker 1952) and are distinguished from partly oxidized magnetite (so-called martitized magnetite) by the even distribution of lamellae of uniform width in the intergrowths. The proportion of magnetite to hematite may be such that abnormally high temperatures of crystallization must be invoked if the ore mineral is assumed to have crystallized as an $Fe_3O_4 . \alpha Fe_2O_3$ solid solution.

As might be expected between end-members of the same type of structure solid solution is complete between Fe_3O_4 and γFe_2O_3 and Hägg (1935, p. 97) demonstrated a steady and continuous fall in cell dimensions from Fe_3O_4 to γFe_2O_3. There is no evidence of exsolution of the γFe_2O_3 on cooling and upon low temperature oxidation of magnetite the progressive change $Fe_3O_4 \rightarrow \gamma Fe_2O_3$ is accompanied by a regular fall in cell dimensions. The magnetic properties of this series are not well known and data is too fragmentary to indicate whether they vary linearly with composition. Since the change from Fe_3O_4 to γFe_2O_3 only involves a replacement of $3Fe^{++}$ in 6-fold co-ordination by $2Fe^{+++}$ they might be expected to do so.

Maghemites have been reported, especially from the Bushveldt igneous complex of South Africa, which contain considerable titanium (Schwellnus and Willemse 1943, Wagner 1928) and it has been suggested that the titanium is trivalent and that Ti_2O_3 may exist in a cubic γ form isomorphous and miscible with γFe_2O_3. Reported analyses of titanomaghemites contain significant amounts of FeO, interpreted as the product of reduction of Fe_2O_3 in the course of oxidation of Ti_2O_3 to TiO_2 during the initial chemical attack of the analytical procedure. But there seems no reason to doubt the possible presence of Fe^{++} and Ti^{++++} in titanomaghemites, while Stscherbina (1939) in discussing the significance of oxidation potentials in geochemistry gave good reasons why considerable concentrations of Ti^{+++} and Fe^{+++} are unlikely to be found together in the same mineral. An interpretation of titanomaghemites as solid solutions between γFe_2O_3, TiO_2 and a cubic $Fe^{++}Ti^{++++}O_3$ would accord better with the oxidation potentials. The hypothetical cubic form of $FeTiO_3$ postulated to be in solid solution with γFe_2O_3 will be referred to as $\gamma FeTiO_3$ and stands in the same relationship to ilmenite that γFe_2O_3 does to hematite. It may be regarded as a γFe_2O_3 type of structure with Fe^{++} Ti^{++++} in place of $2Fe^{+++}$. This replacement in the γFe_2O_3 structure would be expected to result in an increase in the cell dimensions while simple replacement of Fe^{+++} (ionic radius 0·67 Å) by Ti^{+++} (ionic radius 0·69 Å) would have a very slight effect. Basta (1953, p. 77) measured the cell dimension of a titanomaghemite from Bon Accord in the Transvaal with 19·45% TiO_2 and found $a=8{\cdot}3475\pm0{\cdot}001$ Å (cf. maghemite $a=8{\cdot}322$ Å) an observation which tends to support the interpretation of titanomaghemites as $\gamma Fe_2O_3 . TiO_2 . \gamma FeTiO_3$ solid solutions.

No data is available on the magnetic properties of titanomaghemites.

The conditions determining whether the phase crystallizing from a melt intermediate in composition between Fe_3O_4 and Fe_2O_3 will be an $Fe_3O_4 . \gamma Fe_2O_3$ or an $Fe_3O_4 . \alpha Fe_2O_3$ solid solution are unknown, but it is possible that it is always the former and that relatively slow cooling or reheating (as in metamorphism) may allow the Fe_2O_3 to segregate and exsolve as the more stable αFe_2O_3 form. Rapid cooling down to low temperatures (of the order of 250°C) may be necessary for the preservation of the $Fe_3O_4 . \gamma Fe_2O_3$ solid solution.

The $Fe_3O_4 . FeTiO_3$ *Series*

Intergrowths of a spinel ore mineral of the Fe_3O_4–Fe_2TiO_4 series with a rhombohedral ore of the ilmenite–hematite range are commonly found in natural rocks, especially slowly cooled igneous ones. By some authors Ramdohr 1926, Ödman 1932, Newhouse 1936, Edwards 1938) these intergrowths are attributed to exsolution of solid solutions between Fe_3O_4 and $FeTiO_3$. Others (Goldschmidt 1926, Foslie 1928, Mogensen, 1946, Basta 1953) suggest that solid solution between these compositions should be very restricted and interpret the intergrowths by alternative mechanisms such as the exsolution of an Fe_3O_4–Fe_2TiO_4 solid solution followed by a breakdown of the Fe_2TiO_4 component into $FeTiO_3$ and FeO. The 'freezing' of the process at an intermediate stage in some cases is explained by Mogensen (*op. cit.*, p. 588) on the assumption that the excess FeO, if not removed, counteracts any further decomposition of Fe_2TiO_4.

Attempts to synthesize intermediate solid solutions by heating finely powdered magnetite–ilmenite intergrowths or mixtures of magnetite and ilmenite are not usually successful even though temperatures of 1100°C may be maintained for 48 hours (Basta, *op. cit.*). Basta concluded (p. 129 of his thesis) that at the temperature of formation of igneous rocks there is very limited miscibility between magnetite and ilmenite, the limit of solid solution being less than 5% of either end member in the other at 1050°C. This might be atrributed to the difficulty of accommodating the rhombohedral ilmenite lattice in the cubic magnetite (Goldschmidt, *op. cit.*).

Chevallier and Girard (1950) have synthesized cubic solid solutions intermediate between Fe_3O_4 and $FeTiO_3$ up to 37 molecular % $FeTiO_3$. They were optically isotropic with a reflective power of the order of

20% and although the cell dimensions were not accurately determined they are believed to be very similar to magnetite. The method of synthesis adopted by these authors is rather involved but differs fundamentally from earlier attempts in that molten borax was used as a solvent for the iron and titanium oxides so that the crystals prepared formed from a melt. They may represent a meta-stable condition that cannot be synthesized by heating solid mixtures of ilmenite and magnetite. The hypothetical $\gamma FeTiO_3$, already invoked to explain the titanomaghemites, might be expected to enter into solid solution with Fe_3O_4 quite readily. Just as a wide range of solid solution is possible between Fe_3O_4 and γFe_2O_3 although it is very restricted between Fe_3O_4 and αFe_2O_3, so solid solution may occur between Fe_3O_4 and $\gamma FeTiO_3$ although Fe_3O_4 and ilmenite are practically immiscible.

In Chevallier and Girard's preparations ilmenite, hematite, rutile, pseudo-brookite and 'ferromagnetic ilmenite' were formed in addition, but after magnetic separation the $Fe_3O_4 . FeTiO_3$ solid solutions were analysed and their magnetic properties determined with the results given in table 4. The Curie Points were not well defined and the ferromagnetism disappeared over an interval of as much as 150°. The intensity of magnetization varies linearly with composition becoming zero at approx. 30% Fe_3O_4, 70% $FeTiO_3$ if extrapolated beyond the limit of solid solution. From this it is possible, assuming antiferromagnetism in a hypothetical solid solution of this composition and the perfect magnetic structure for magnetite, to predict a possible distribution of ions among the cation positions of $\gamma FeTiO_3$ on the basis of a defect spinel structure comparable to γFe_2O_3. Allowing for slight errors in the extrapolation and assumptions made it appears probable that in the perfect structure for $\gamma FeTiO_3$ all the f positions would be filled by Fe^{++} and all the Ti^{++++} would be in c positions as in ulvospinel. The proportion of Ti^{++++} to Fe^{++} in the c positions would be 4 : 1 so that successive cation layers would be largely made up of Fe^{++} ions and then largely Ti^{++++} ions (cf. ilmenite). By analogy with γFe_2O_3 we might predict that such a structure would be

Table 4. Magnetic Properties of the $Fe_3O_4 . FeTiO_3$ Series of Solid Solutions (after Chevallier and Girard 1950)

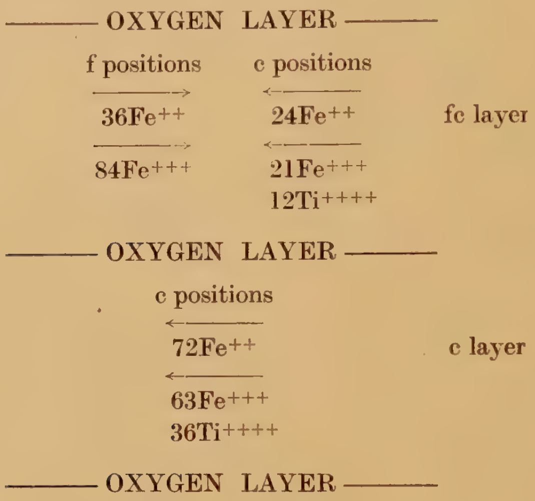
% Fe_3O_4	100	90	85	78	71	63
Curie Point·°c	580		540	500	450	405
Intensity of magnetization at 20° in a field of 6500 gauss*	90	82	71	61·5	52·5	435

* Practically equal to the intensity of saturation magnetization.

ferrimagnetic with an intensity of saturation magnetization of *ca.* 65 e.m.u./g. In all solid solutions between Fe_3O_4 and $\gamma FeTiO_3$ with a perfect intermediate structure the titanium would be restricted to the c positions and thus distributed between the fc and c cation layers in the proportion 1 : 3 (fig. 11).

Fig. 11

Distribution of cations/480 anions



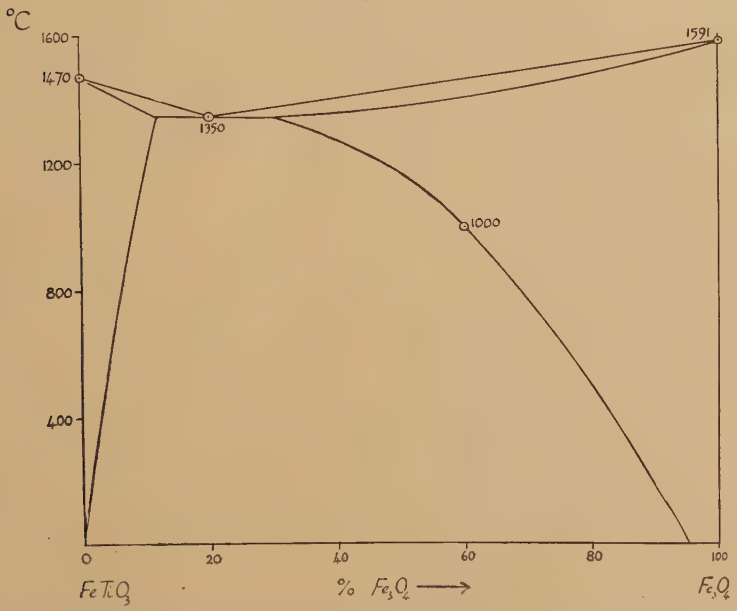
perfect structure
$70\%Fe_3O_4$ $30\%Fe_{4/3}Ti_{4/3}O_4$
$(64\%Fe_3O_4$ $36\%FeTiO_3)$

Diagrammatic magnetic structure for a solid solution of composition 64% Fe_3O_4, 36% $\gamma FeTiO_3$ (the composition which according to Chevallier and Girard's (1950) figures has an intensity of magnetization in a field of 6500 gauss half that of pure magnetite). The numbers of cations in the two different types of cation layer of the spinel structure are shown and in the fc layer the distribution of the ions between the two kinds of position. Arrows indicate the direction of the magnetic moments.

It is improbable that solid solution is continuous between Fe_3O_4 and $FeTiO_3$ at the temperatures at which natural rocks form. From the diagram of stability fields in the dry system FeO–Fe_2O_3–TiO_2 (Ernst 1943) a fall of the liquidus from both ends of the pseudobinary system $Fe_3O_4 . FeTiO_3$ may be deduced and the probable form of the phase diagram under dry conditions is shown in fig. 12. In the presence of volatiles, as during the formation of natural rocks, the liquidus and solidus may be depressed, thus restricting the maximum range of possible solid solution.

Since solid solution is continuous between Fe_3O_4 and Fe_2TiO_4 and may be expected to be theoretically possible between γFe_2O_3 and $\gamma FeTiO_3$, the $Fe_3O_4 . FeTiO_3$ solid solutions should perhaps be regarded as intermediates between these two series and merely representative of a range of solid solutions of the same general type but with compositions not necessarily on the direct $Fe_3O_4 . FeTiO_3$ join. The exsolution of such solid solutions on slow cooling would then depend on the form of the solvus surface over the field $Fe_3O_4 . FeTiO_4 . FeTiO_3 . Fe_2O_3$. Very little data is available on the precise position of this surface, but it probably has a similar form to that indicated by the contouring of fig. 13, and a description of the exsolution of a solid solution 70% Fe_3O_4 . 30% $FeTiO_3$ based on this diagram should not be seriously in error. At a temperature

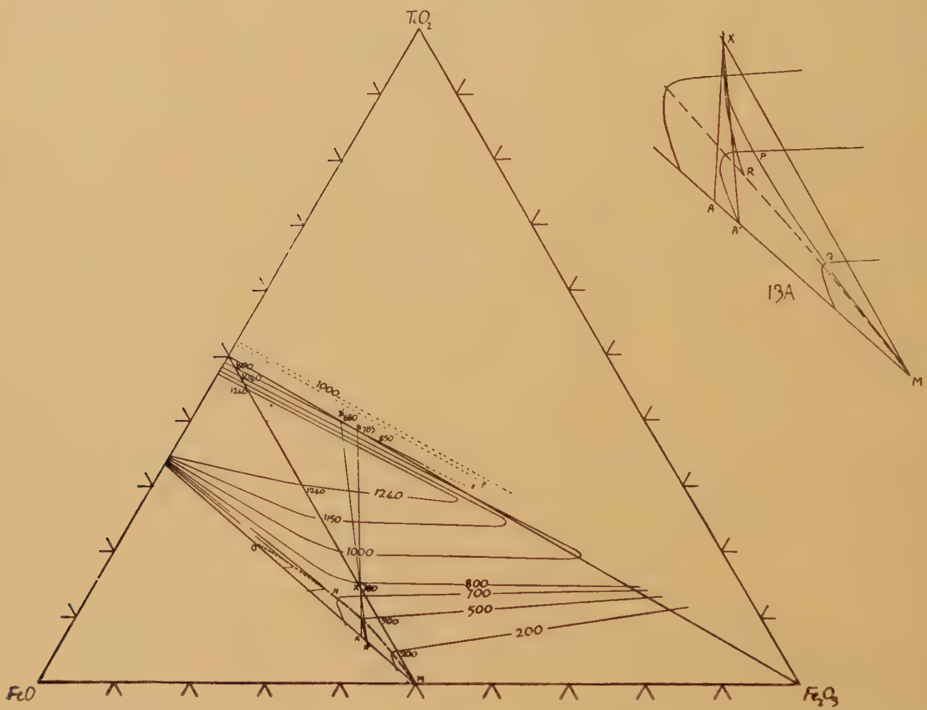
Fig. 12



Probable form of the phase diagram of the dry pseudo-binary system $Fe_3O_4 . FeTiO_3$. The form of the solvus is probably substantially correct but its position is not known with any precision.

of *ca.* 780°c the single phase would separate into a spinel and a phase intermediate in composition between $FeTiO_3$ and Fe_2O_3 which at this temperature would be a rhombohedral form (even if it initially separates as a cubic γ-form inversion to the rhombohedral form would be very rapid at a temperature of 780°c). The probable composition for the first formed spinel is that which involves the least relative disturbance of the existing distribution of cations especially those in the f positions and will tend to lie therefore on, or close to the join 70% Fe_3O_4 . 30% $FeTiO_3$ to 70% Fe_3O_4 . 30% Fe_2TiO_4. Projected to cut the $FeTiO_3 . Fe_2O_3$ join this construction gives 65% $FeTiO_3$ 35% Fe_2O_3 as the composition of the rhombohedral phase. At 780°c this composition is represented by an intergrowth of two rhombohedral phases, not one. The nearest composition which at 780°c could be represented by a single rhombohedral phase is 77% $FeTiO_3 . 23\% \ Fe_2O_3$ and this will be the composition of the exsolved phase at this temperature, the spinel host changing in composition towards 77% $Fe_3O_4 . 23\% \ Fe_2TiO_4$ (tie line AB of fig. 13). As the temperature falls and exsolution proceeds the composition of the stable rhombohedral phase becomes progressively enriched in $FeTiO_3$ and the spinel enriched in Fe_3O_4 (curve XPQM of fig. 13A). Thus at 680°c the rhombohedral phase has the composition 80% $FeTiO_3 . 20\% \ Fe_2O_3$ and the spinel is intermediate between 70% $Fe_3O_4 . 30\% \ FeTiO_3$ and 80% $Fe_3O_4 . 20\% \ Fe_2TiO_4$ (tie line A′B′ of fig. 13). Two alternatives are possible :—

Fig. 13



Probable form of the solvus surface in the system $Fe_3O_4 . Fe_2TiO_4 . FeTiO_3 . Fe_2O_3$. The 1150°c contour encloses an area of compositions unlikely to crystallize as homogeneous phases from igneous rocks and thus represents an 'area of immiscibility' for natural solid solutions of this system.

13A Enlargement of part of the diagram near M (Fe_3O_4) to illustrate exsolution of an $Fe_3O_4 . FeTiO_3$ solid solution X (see text).

(1) The first formed rhombohedral phase itself exsolves at lower temperatures into a hematite–ilmenite intergrowth.

(2) Continued exsolution is accompanied by an ionic exchange $2Fe^{+++} \rightleftharpoons Fe^{++} + Ti^{++++}$ between the cubic and rhombohedral lattices so that the latter always conforms to the composition of a single stable phase at the temperature in question. The second alternative requires equilibrium to be more fully maintained and involves a continuous reaction expressed empirically by

$$Fe_6^{+++}Fe_5^{++}TiO_{16} + Fe_2^{+++}Fe_3^{++}Ti_3O_{12} \rightarrow Fe_8^{+++}Fe_4^{++}O_{16} + Fe_4^{++}Ti_4O_{12}$$

$$(75\%\ Fe_3O_4 . 25\%\ Fe_2TiO_4)(75\%\ FeTiO_3 . 25\%\ Fe_2O_3).$$

With sufficiently slow cooling this trend of double compositional variation will be maintained and eventually the intergrowth may consist of nearly pure ilmenite intergrown with nearly pure magnetite.

In this discussion it has been assumed that the rhombohedral phase will have a composition truly intermediate between $FeTiO_3$ and Fe_2O_3. The exceedingly steep slope of the solvus near the join $FeTiO_3$–Fe_2O_3 for compositions in the region of 100% $FeTiO_3$ to 60% $FeTiO_3$. 40% Fe_2O_3 makes it improbable that they will carry an excess of FeO but natural rhombohedral ore minerals often carry an excess of TiO_2. It may be that the deep ‘ valley ’ in the solvus surface extending into the ternary system FeO–Fe_2O_3–TiO_2 from $FeTiO_3$ may not run straight along the $FeTiO_3$–Fe_2O_3 join but may trend to the TiO_2-rich side of it. In this event the rhombohedral phase first exsolved from the 70% Fe_3O_4 . 30% $FeTiO_3$ solid solution may differ slightly in composition from the 77% $FeTiO_3$. 23% Fe_2O_3 suggested above being richer in Fe_2O_3 and containing a slight excess of TiO_2 but the subsequent course of exsolution would be essentially similar to that outlined here.

Attempts to homogenize the intergrowths by heating are unlikely to be successful for two reasons :—

(1) The continuous reaction which brought the magnetite and ilmenite into existence would have to be reversed so that the composition pair formed during the initial exsolution would be reformed. This would require long continued heating at sufficiently high temperatures for ionic migration to produce appreciable effects but there is some indication (in the cell dimension changes of the component phases reported by Basta (1953, p. 128)) that this sort of change does take place on heating.

(2) The solid solutions from which the intergrowths formed are probably metastable intermediates between magnetite and a cubic form of $FeTiO_3$ ($\gamma FeTiO_3$) which cannot be produced by heating rhombohedral $FeTiO_3$ (ilmenite).

Failure to homogenize these intergrowths cannot therefore be accepted as evidence against the existence of $Fe_3O_4 . FeTiO_3$ solid solutions, the reality of which would appear to be in question no longer.

The nature of the rhombohedral phase, the exsolution of which from a cooling solid solution involves the minimum displacement of cations, may be deduced on the assumption that the $Fe_3O_4 . FeTiO_3$ solid solution has the structure here suggested and the exsolved spinel has the perfect structure of the $Fe_3O_4 . FeTiO_3$ series. It proves to be a 'substituted hematite'. The exsolution of a solid solution 70% Fe_3O_4 30% $FeTiO_3$ into 70% spinel (80% $Fe_3O_4 . 20\% \ Fe_2TiO_4$)* and 30% rhombohedral phase yields a ferrimagnetic 'substituted hematite' with the proportions of Fe^{+++}, Fe^{++} and Ti^{++++} different in successive cation layers. In one of the simplest possibilities successive cation layers contain 118 Fe^{+++}, 21 Fe^{++}, 21 Ti^{++++} and 34 Fe^{+++} 63 Fe^{++} 63 Ti^{++++} per 480 oxygen ions. With continued exsolution the rhombohedral phase would approach much more nearly to an ordered condition in which the proportions of ions were similar in all cation layers and thus become less ferrimagnetic. The disordered distribution of cations and the consequent ferrimagnetism may be regarded as an 'inherited' characteristic likely to be lost as greater equilibrium of distribution of cations is attained. This seems to be the most probable mode of origin for the ferrimagnetic rhombohedral minerals. It becomes possible if the ore mineral is cooled slowly after its first formation until exsolution begins to take place and is then rapidly chilled so that the 'inherited' disordered distributions of ions in the rhombohedral lattice is preserved. The best known example of a ferrimagnetic rhombohedral ore mineral is that described from the Haruna dacite pumice (Nagata, Akimoto and Uyeda 1953 and earlier papers) for which a cooling history similar to this may be deduced from the petrographic evidence. The ore fraction from this rock contains a cubic ore mineral, the rhombohedral ore mineral mentioned and composite grains of the two in different proportions. The existence of the latter supports the view that some at least of the rhombohedral phase may originate by exsolution and owe its ferrimagnetic character to an 'inherited' disordered distribution of cations as suggested here.

The fragmentary data does not permit the solvus of the Fe_3O_4–Fe_2TiO_4–$FeTiO_3$–Fe_2O_3 system to be plotted with any precision in the critical Fe_3O_4-rich part of the field. The existence of intergrowths of two spinels of the Fe_3O_4–Fe_2TiO_4 series indicates however a sudden change of slope of this surface near the Fe_3O_4–Fe_2TiO_4 join so that there is a narrow field of composition here embracing solid solutions which will exsolve to such intergrowths instead of spinel-rhombohedral phase intergrowths. It is illustrated qualitatively in fig. 13 (field MNO). The existence of two fields, one of compositions exsolving to a spinel and a rhombohedral phase, and the other of compositions exsolving to two spinels, implies a theoretical possibility of an intergrowth of three ore minerals arising from the exsolution of solid solutions of compositions lying on the field boundary. Such compositions might be attained by the spinel component of a spinel-rhombohedral phase intergrowth, if exsolution occurred under cooling conditions such that equilibrium was not fully maintained and the rhombohedral phase was not brought to a uniform composition at all temperatures by the ionic migrations mentioned earlier. The curve followed by the trend of composition in the spinel would then have the form of XR in fig. 13 A during exsolution of the rhombohedral phase alone but from R onwards two phases, a second spinel and the rhombohedral phase would be exsolved simultaneously.

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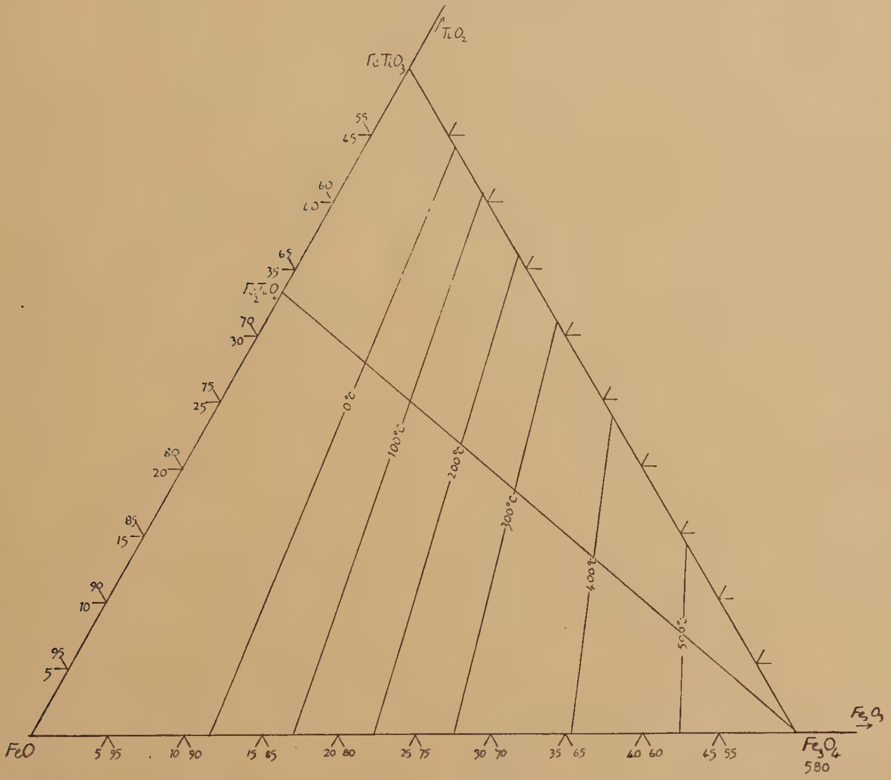
* In view of the uncertainty concerning the true position of the solvus the composition of the first-formed spinel was taken to the nearest 10% Fe_3O_4 for calculation purposes.

Fig. 14



Variation of Curie Point with composition in the system $Fe_3O_4 . Fe_2TiO_4 . FeTiO_3$ after Chevallier and Girard (1950). Lines of equal Curie Points are plotted at 100° intervals.

Chevallier and Girard (1950) published a diagram illustrating the variation in Curie Point with composition in the system Fe_3O_4–Fe_2TiO_4–$FeTiO_3$ (reproduced as fig. 14). They suggest that the Curie Point variation may be expressed by

$$\theta°\text{K (Curie Point)} = 1245s \qquad \text{where} \qquad s = \frac{\text{wt.\% } Fe_2O_3}{\text{wt.\% } Fe_2O_3 + FeO}.$$

Any such theoretical treatment assumes a constant degree of order in the ores considered which may be justified for artificial preparations but is not necessarily so for natural ores forming under different physical conditions. Nevertheless it is clear from the trend of Chevallier and Girard's lines of equal Curie Points that exsolution (or homogenization) of ores whose composition lies within this field could significantly change their Curie Points and related magnetic properties. The general validity of the basic assumption, that in titaniferous magnetites the Curie Point and saturation magnetization are governed by the concentration of Fe_3O_4 in the material, whatever the nature of the other oxides in solid solution, is shown by the comparisons made by Chevallier, Mathieu and Vincent (1954). They compared percentages of Fe_3O_4 in a series of ores determined from analytical data and deduced from magnetic measurements. Curie Point determinations were used to evaluate the percentage of Fe_3O_4 in the ferromagnetic spinel element of the titaniferous magnetite and the saturation magnetization of this element. The saturation magnetization of the ore as a whole was expressed as a percentage of that of the ferromagnetic spinel element, this percentage being that of the ferromagnetic spinel in the ore. From this figure and that for the percentage of Fe_3O_4 in the ferromagnetic spinel the percentage of Fe_3O_4 in the ore was deduced. Table 5 shows the figures obtained on eight ores from Greenland gabbros analysed by Vincent, which are in good agreement in view of the somewhat arbitrary nature of the recalculation of the analyses.

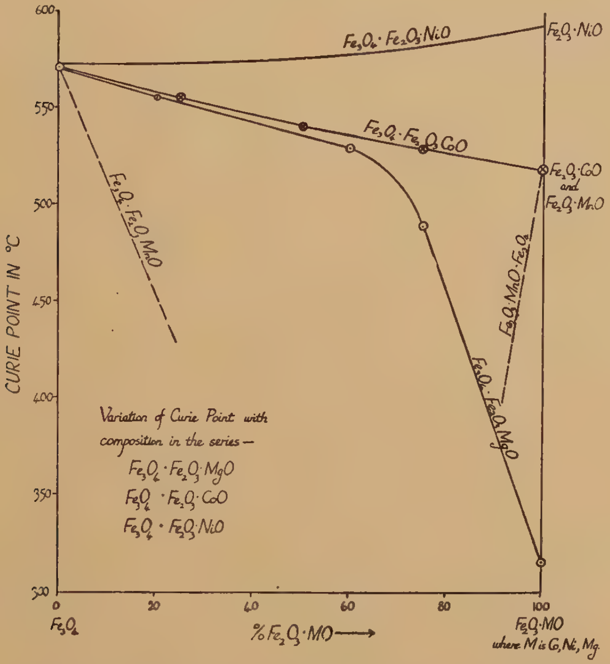
Table 5

Specimen	% Fe_3O_4 deduced from magnetic measurements	% Fe_3O_4 calculated from chemical analysis
1	51·5	56·0
2	37·2	35·3
3	55·3	57·3
4	60·0	59·7
5	40·5	39·9
6	63·1	61·5
7	37·6	41·8
8	54·2	55·3

§ 4. EFFECT OF OTHER CATIONS IN THE STRUCTURE OF THE IRON OXIDES

Analyses of natural magnetites show that they frequently contain other cations as well as Fe^{+++}, Fe^{++} and Ti^{++++}, e.g., Mg^{++}, Mn^{++}, Al^{+++} and V^{+++}, the presence of which may modify the magnetic properties of the oxide. Variations of Curie Point and cell dimensions in substituted magnetites have been summarized by Michel, Chaudron and Bénard (1951). Magnetite is a ferrite (a group of compounds of general formula $Fe_2O_3 . MO$ where M represents Fe^{++}, Mn^{++}, Mg^{++}, Co^{++}, Ni^{++}, Zn^{++} etc.) and enters into complete series of solid solutions with other ferrites of similar structure in which the ionic radius of M is less than that of Fe^{++} (Bénard 1939, p, 88), e.g., Fe_2O_3 . CoO. The variation of Curie Point in these series is illustrated in fig. 15, that of cell dimensions in fig. 16. In mixed ferrites, i.e., those containing a number of different divalent ions the total effect of the replacement is a summation of their individual effects considered separately if the foreign ions enter the same lattice sites (6-fold co-ordinated c positions) as those normally occupied by Fe^{++}. When the foreign ions tend to enter the 4-fold co-ordinated f positions, as is the case with Zn^{++}, a close correspondence frequently obtains between the observed magnetic properties and those which may be calculated following the hypothesis of Néel on the ferromagnetism of the spinel ferrites (Guillard 1951 a). From fig. 15 it is clear that up to 20% replacement of Fe^{++} by Ni^{++}, Co^{++} or Mg^{++} has little effect on the Curie Point and this extent of replacement is rarely exceeded in natural ores. Exceptionally up to 8% MgO may appear in the analyses, corresponding to 40% $MgFe_2O_4$ but such values are uncommon. Manganese, which has a more pronounced effect, is rarely present in appreciable amount and natural ores usually contain less than 3% MnO corresponding to 10% $MnFe_2O_4$.

Fig. 15

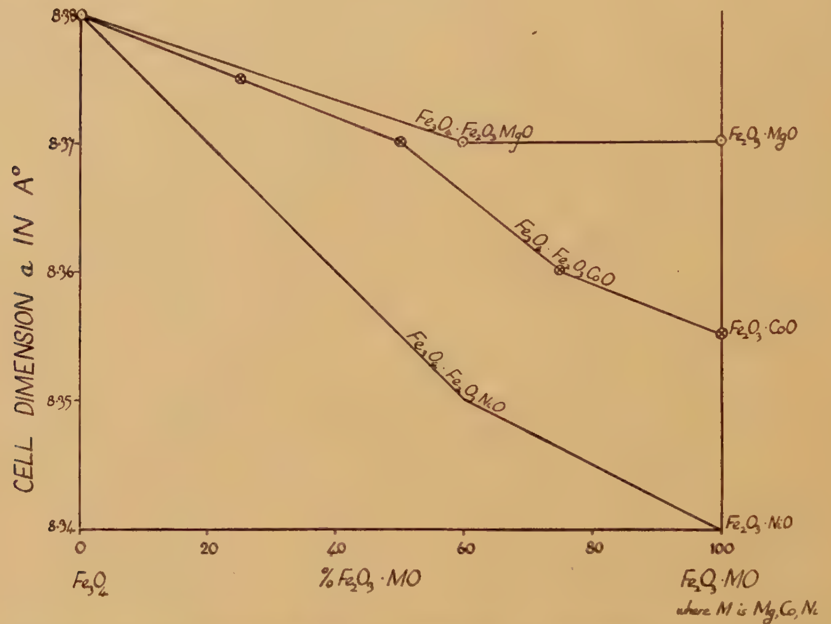


Variation of Curie Point with composition in the series Fe_3O_4–$CoFe_2O_4$, Fe_3O_4–$NiFe_2O_4$ and Fe_3O_4–$MgFe_2O_4$. Data also plotted for Fe_3O_4-rich and $MnFe_2O_4$-rich members of the Fe_3O_4–$MnFe_2O_4$ series.

Even so it is apparent that the two divalent ions most likely to occur in amount sufficient to affect the magnetic properties of natural ores will both cause a lowering of the Curie Point. Zinc has been determined in ores from various Greenland gabbros by Vincent (Phillips and Vincent 1954, p. 12) but the maximum recorded content of 1700 parts per million is still too low for it to have any appreciable effects on the magnetic properties of these minerals.

Replacement of Fe^{+++} in magnetite by other trivalent ions e.g., Al^{+++}, Cr^{+++} and V^{+++} also occurs. The effect of Al^{+++} and Cr^{+++} in the magnetite lattice on the Curie Point and cell dimensions is shown in fig. 17 : the effect of V^{+++} is not known. Up to *ca.* 15% of the Fe^{+++} ions may be replaced by Al^{+++} (Michel and Pouillard 1948) and up to 18% of the Fe^{+++} ions by Cr^{+++} (Pouillard 1950). Contents of Al_2O_3 of up to 7% have been recorded in natural magnetites corresponding to replacement of 11–12% of the Fe^{+++} ions. Contents of Cr_2O_3 and V_2O_3 are usually too low for replacement of Fe^{+++} by Cr^{+++} or V^{+++} to have influenced the Curie Points of natural ores significantly. Cr_2O_3 is usually less than 0·5% and V_2O_3 rarely exceeds 2% corresponding to replacement of less than 3% of the Fe^{+++} ions by V^{+++}. But as with the replacement of Fe^{++} by divalents such replacement of Fe^{+++} as occurs in natural ores is likely to lower the Curie Point below the value for pure Fe_3O_4.

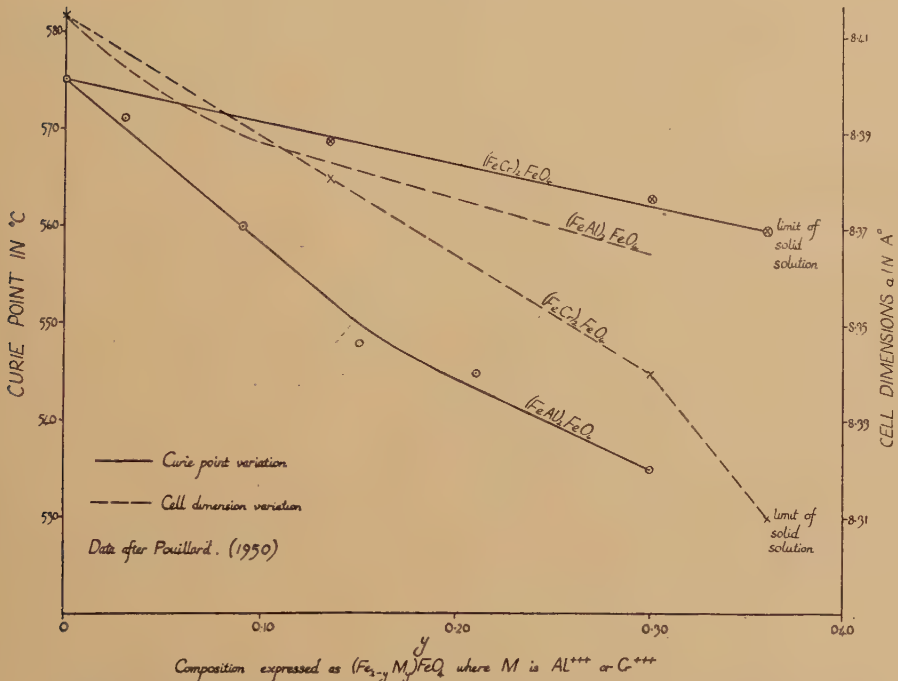
Fig. 16



Variation of cell dimensions with compositions in the series Fe_3O_4–$CoFe_2O_4$, Fe_3O_4–$NiFe_2O_4$ and Fe_3O_4–$MgFe_2O_4$.

Synthetic ferrites have been prepared in which Na^+ and Fe^{+++} replace $2Fe^{++}$ in the magnetite structure but the limit of replacement is low ; less than 7% of the Fe^{++} ions can be replaced. Such replacement causes the Curie Point to fall from 575° to 535° and the cell dimension to rise from 8·41 to 8·43 (Michel 1937, p. 371). Significant contents of Na_2O have not been reported from naturally occurring oxide ores.

Fig. 17



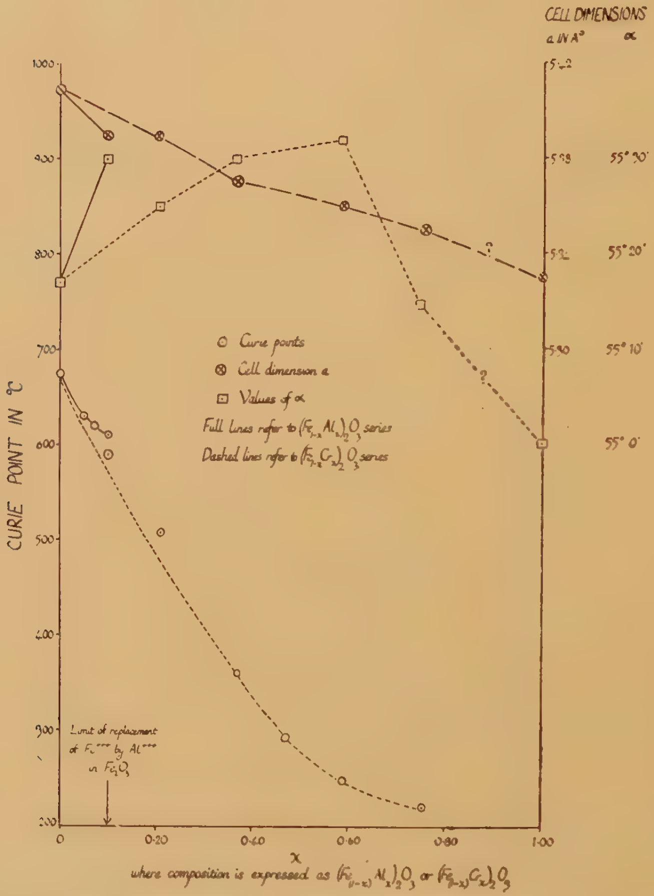
Variation of Curie Point and cell dimension with composition in Al- and Cr-bearing magnetites.

Replacement of Fe^{+++} by Al^{+++} and Cr^{+++} also occurs in hematite with the effects on Curie Point and cell dimensions shown in fig. 18. Substitution of Fe^{+++} by Al^{+++} is restricted to a 10% replacement but complete substitution of Fe^{+++} by Cr^{+++} probably occurs (Pouillard 1950). Natural hematites, however, often correspond very closely in composition to Fe_2O_3 or Fe_2O_3–$FeTiO_3$ solid solutions with insignificant amounts of foreign ions (other than Ti^{++++}) present.

The maghemite structure, being a defect spinel structure, is subject to invasion by foreign ions as well as replacement. Bénard (1939, p. 82) showed that oxidation of a substituted magnetite containing Mg to the extent of $FeO/MgO=4$ yielded a Mg-bearing γFe_2O_3 with a Curie Point of 610°. This compound may be regarded as an intermediate between γFe_2O_3 and $Fe_2O_3 . MgO$. Intermediates between γFe_2O_3 and

$Fe_2O_3 . MnO$ may be produced similarly provided that the content of $Fe_2O_3 . MnO$ in the original substituted magnetite exceeds 25%. The variations of Curie Point with composition in the series γFe_2O_3–$Fe_2O_3 . MgO$ and γFe_2O_3–$Fe_2O_3 . MnO$ are shown in fig. 19. The oxidation of Fe_3O_4–$Fe_2O_3 . MgO$ solid solutions becomes more difficult with

Fig. 18



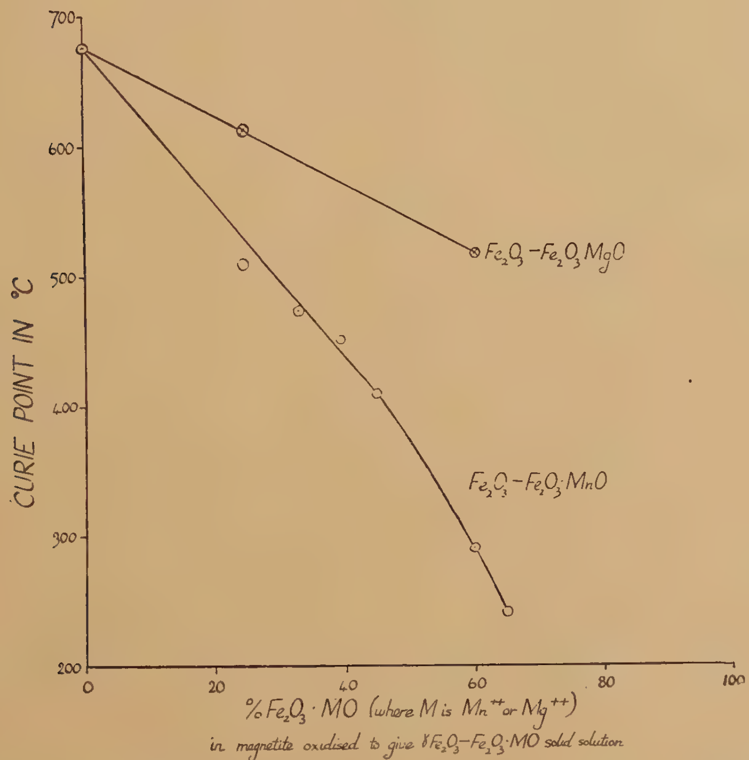
Variation of Curie Point and cell dimension with composition in Al- and Cr-bearing hematites.

increasing content of Mg and, although the introduction of Mg atoms into the structure of γFe_2O_3 makes the latter more stable, $Fe_2O_3 . MgO$-rich members of the γFe_2O_3–$Fe_2O_3 . MgO$ series cannot be prepared by this method since the temperature to which the specimens must be heated for oxidation to occur exceeds the temperature at which the $\gamma Fe_2O_3 . Fe_2O_3 . MgO$ solid solution decomposes. Oxidation of Fe_3O_4–$Fe_2O_3 . MnO$ solid solutions is always relatively easy but when the

FeO/MnO ratio falls below 1 secondary reactions take place with the formation of MnO_2 and the Mn-rich members of the γFe_2O_3–$Fe_2O_3 . MnO$ series are not obtained. These maghemite–ferrite solid solutions have the basic structure of spinels.

Replacement of Fe^{+++} in maghemite by Al^{+++} takes place up to a limit of 10% at ordinary temperatures (Pouillard 1950). The Al-bearing maghemites are more stable than pure γFe_2O_3 the temperature of rapid inversion rising from 200–300°c, for pure γFe_2O_3 to 650° when 7% of the Fe^{+++} is replaced by Al^{+++}. The extent of possible replacement of Fe^{+++} by Al^{+++} rises rapidly with increasing temperature and crystals with up to 32% Al_2O_3 present can be preserved by chilling from a temperature of 625°. The variations of Curie Point and cell dimensions with composition in these Al-bearing maghemites are illustrated in fig. 20. Cr^{+++} does not appear to replace Fe^{+++} in γFe_2O_3 in artificial preparations and only to a slight degree in natural maghemites (less than 0·5%). V^{+++} has been

Fig. 19

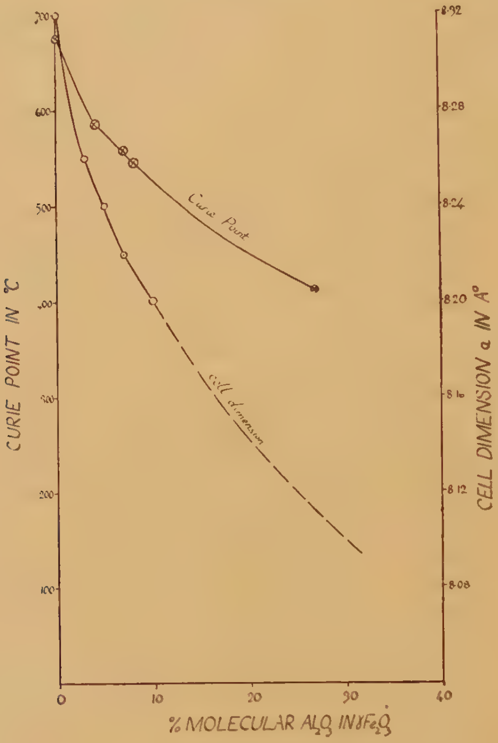


Variation of Curie Point with composition in the series γFe_2O_3–$MgFe_2O_4$ and γFe_2O_3–$MnFe_2O_4$, members of which are produced in the laboratory by oxidizing 'substituted' magnetites.

reported as high as 2·40% V_2O_3 in natural titanomaghemite from the Transvaal (Basta 1953) but no data is available on the effect of replacement of Fe^{+++} by V^{+++} on the magnetic properties of γFe_2O_3.

The existence of magnetite–ferrite solid solutions and substituted magnetites in which Fe^{+++} is replaced by Al^{+++}, Cr^{+++} or V^{+++}, of magnetite–ulvöspinel solid solutions, of a complete range of possible solid solution between magnetite and maghemite, of maghemite–ferrite solid solutions and substituted Al^{+++}- or V^{+++}-bearing maghemites all with the same basic structure—the spinel structure—indicates how wide is the possible range of composition for ferrimagnetic oxide minerals of the spinel group. Natural ferrimagnetic spinels however, occupy only a small part of it.

Fig. 20



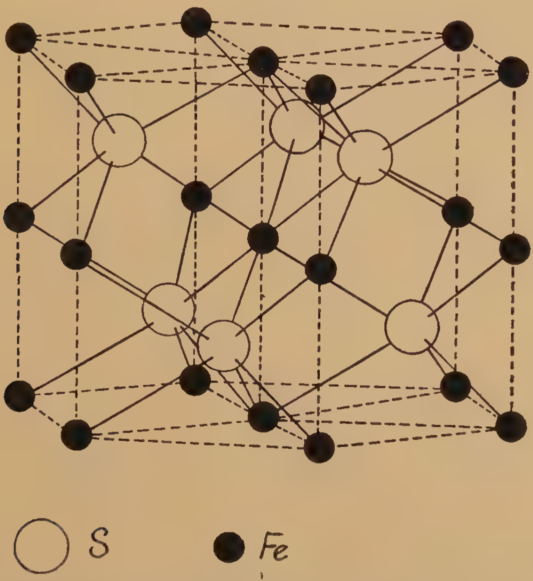
Variation of Curie Point and cell dimension with composition in Al-bearing maghemites.

The effect of foreign ions in the structure of FeO–Fe_2O_3–TiO_2 solid solutions on their exsolution is not known. A study of the relationship exhibited by natural ores, e.g. those of Skaergaard, East Greenland (Phillips and Vincent 1954), suggests that the field of composition of solid solutions exsolving into two spinels is more extensive if these solid solutions contain other cations as well as Fe^{++}, Fe^{+++} and Ti^{++++}. But data on the ore minerals is still too fragmentary for this to be more than a suggestion, and the observed facts may be interpreted in other ways (see p. 171 of this paper).

§ 5. THE FERRIMAGNETIC SULPHIDE MINERALS

Of the iron sulphides troilite (FeS), pyrites ($\mathrm{FeS_2}$) and pyrrhotite (usually written $\mathrm{FeS}_{(1+x)}$ though, in view of its structure, better written $\mathrm{Fe}_{(1-y)}\mathrm{S}$) the latter alone is ferrimagnetic. Its composition is variable, x varying between 0 and 1·14 for temperatures about 300°c (Roberts 1935, p. 1037) and between 0 and 0·25 at 650°c (Hägg and Sucksdorf 1933, p. 448). Nagata (1953 a, p. 33) quotes its magnetic properties to be :—Curie Point 300∼325°c, saturation magnetization$\simeq$62 e.m.u./cm^3, but they are known to vary with composition.

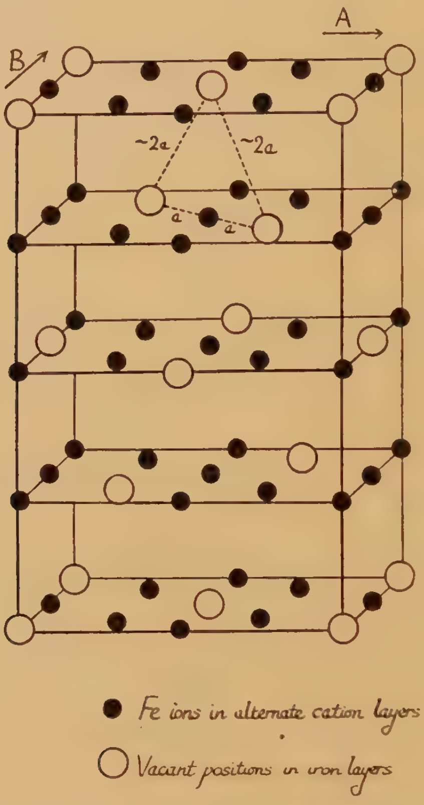
Fig. 21



The structure of troilite, FeS (after Bragg's figure of the structure of NiAs (Bragg 1937, p. 66)). Sheets of sulphur ions alternate with sheets of iron ions—each sulphur ion lies between six irons and each iron between six sulphurs.

FeS is hexagonal with cell dimensions $a=5{\cdot}946$ Å, $c=11{\cdot}720$ Å (Hägg and Sucksdorf, *op. cit.*, p. 446). The iron ions are arranged in layers perpendicular to the hexad axis alternating with layers of sulphur ions (fig. 21). According to earlier workers the same crystal structure extends over the composition range $0<x<0{\cdot}20$ in the pyrrhotites, but recently Bertaut (1952) showed that pyrrhotite was only pseudohexagonal with a monoclinic unit cell $a=11{\cdot}9$ Å, $b=6{\cdot}865$ Å, $c=27{\cdot}72$ Å, $\beta=89°\,33'$; the composition at which the symmetry drops is close to $FeS_{1\cdot 08}$ according to Néel's interpretation of the ferrimagnetism of pyrrhotite. The departure of the composition of pyrrhotite from FeS is a consequence of the omission of iron ions from the structure which further necessitates the replacement of some Fe^{++} ions by Fe^{+++} ions in order that the charge balance of the structure may be preserved. Thus in $FeS_{(1+x)}$ there must be $(1-2x)$ Fe^{++} ions and $2xFe^{+++}$ ions. The vacant positions in the pyrrhotite structure are restricted to alternate iron layers and distributed in such a way as to be as widely dispersed as possible, the distance between any two vacant positions being nearly always approximately $2a$ (fig. 22).

Fig. 22

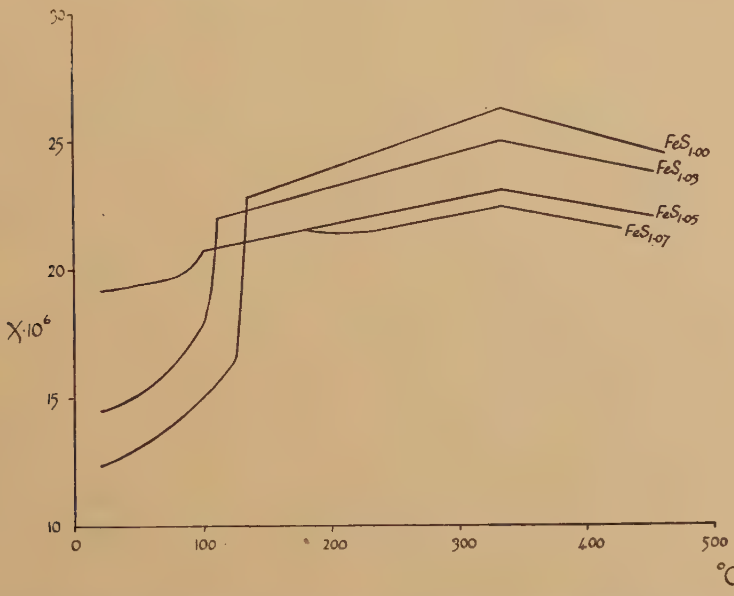

A
B
~2a
~2a
a
a
● Fe ions in alternate cation layers
○ Vacant positions in iron layers

The vacant positions in the pyrrhotite structure, the relative positions of which are indicated here by omitting, for clarity, the sulphur ions and alternate layers of iron ions from the complete structure—after Bertaut (1952). The vacancies are regularly distributed in the iron layers in which they occur.

The magnetic properties of members of the troilite–pyrrhotite series depend on the amount of iron present in the structure. They are said to be antiferromagnetic in the range $0<x<0\cdot 08$ and 'ferromagnetic' beyond

(Néel 1953, p. 60) while FeS is said to be an antiferromagnetic of the classic type (Néel 1953, p. 60). It appears likely that successive planes of iron atoms are magnetized to saturation alternately in opposite directions so that two magnetic sub-lattices can be recognized, one composed of iron layers 1, 3, 5 . . . etc., the other the alternate layers 2, 4, 6 . . . etc. Being crystallographically identical, both in their content and distribution of Fe^{++} ions in pure FeS, these sub-lattices have opposed spontaneous magnetizations which exactly compensate. A weak ferromagnetism (ferrimagnetism ?) with a Curie Point of 600°c has been reported in this compound (Michel, Chaudron and Bénard 1951, p. 196) and may possibly be referred to imperfect compensation of the two lattices on account of structural irregularities or minor discrepancies of composition (cf. hematite). With slight omission of Fe^{++} the Curie Point is said to fall until at $x=0{\cdot}0003$ it is 500°c. In the range $0<x<0{\cdot}8$ the form of the specific susceptibility-temperature curves are as shown in fig. 23. The breaks in these curves may be correlated with phase transformations described by Roberts (1935). Figure 24, reproduced from his data, indicates the temperature stability fields for different ' forms ' of the sulphide based on thermal analyses of synthetic material. One or more of these ' forms ', e.g., e may in reality be a mixture but it seems likely that the rapid reversible bc transformation at 315–318°c and cg transformation at temperatures varying up to 144°c do represent real phase transformations.

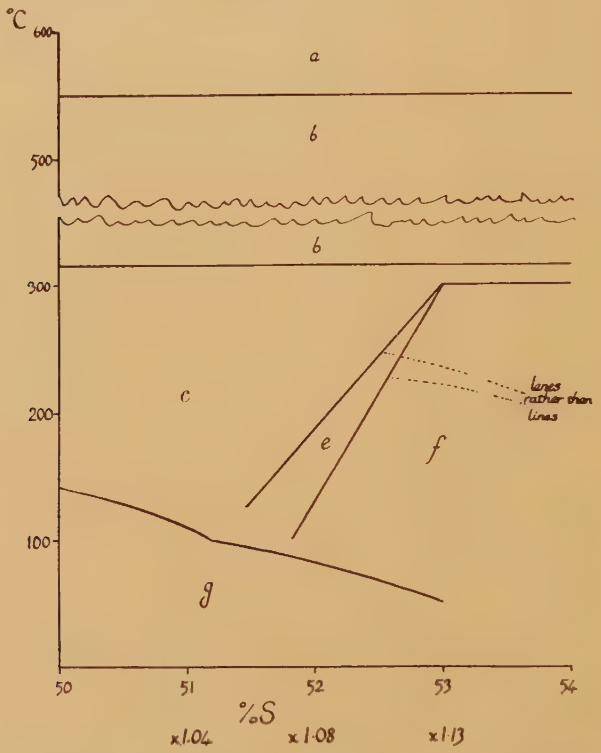
Fig. 23



Variation of specific susceptibility with temperature for sulphides of composition $FeS_{(1+x)}$ where $0<x<0{\cdot}08$—data from Haraldsen (1937).

Néel (1953) quotes Benoit for the information that saturation magnetization in the FeS–$FeS_{(1+x)}$ series is at first very weak but passes through a maximum at about $x=0{\cdot}14$, i.e., $FeS_{1{\cdot}14}$, very close to Fe_7S_8, a frequently reported approximate composition of natural pyrrhotite. These ferrimagnetic sulphides ($x>0{\cdot}09$) have specific susceptibility-temperature curves of the type shown in fig. 25, which are difficult to correlate with the phase diagram (fig. 24) except in so far as the development of ferrimagnetism seems to be associated with the appearance of the field e which may merely represent a sluggish of inversion. The hexagonal axis of pyrrhotite is a direction of difficult magnetization—in the plane perpendicular to this the magnetic symmetry is less than the crystallographic symmetry but in the direction of easiest magnetization the saturation magnetization is so small as to immediately suggest its ferrimagnetic character. The imperfect compensation of the two sub-lattices giving rise to this ferrimagnetism is attributed by Néel (*op. cit.*, p. 61) to the

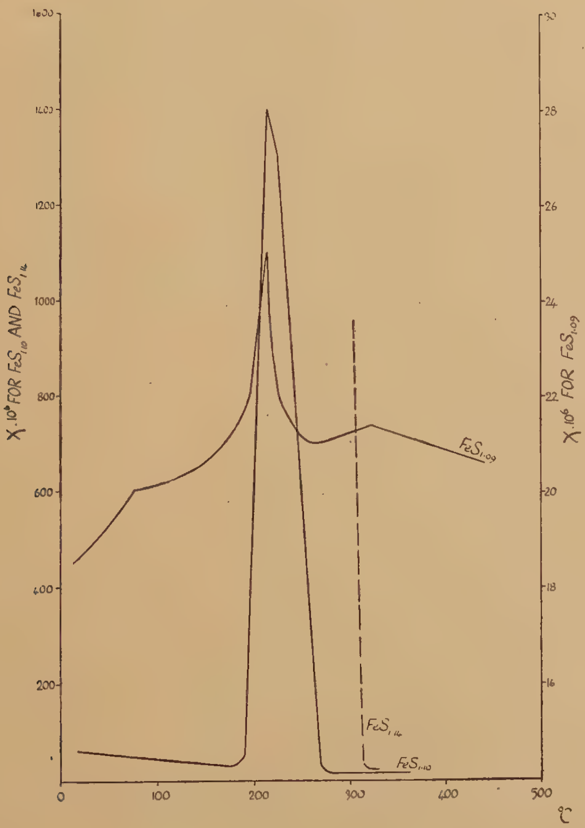
Fig. 24



Stability fields for different 'forms' of sulphides of general composition $FeS_{(1+x)}$ at different temperatures—data from Roberts (1935). Variation of transformation temperatures with composition is indicated by the trend of the lines separating adjacent fields.

distribution of the vacant iron positions on one magnetic sub-lattice only as suggested by Bertaut (fig. 22) and to the distribution of the Fe^{+++} ions in the structure not being such as to negate the effect of the vacancies. A complete quantitative interpretation of the saturation magnetization of pyrrhotite has not yet been given but it is apparent that on this hypothesis ferrimagnetism will only develop if the vacant positions are sufficiently abundant for effective interaction with consequent development of a super-lattice. Where $x < 0{\cdot}08$ the vacant positions are too far apart for this to be so and tend to distribute evenly on all the iron planes, thus leaving the structure essentially antiferromagnetic. The Curie Point of pyrrhotite varies from 270°c for $FeS_{1\cdot 10}$ to 330°c for $FeS_{1\cdot 20}$ (Haraldsen 1937, p. 89) as shown in fig. 26. Above approximately 560°c the susceptibility becomes five or six times smaller and its thermal variation much like that of FeS (Benoit 1952). This seems to correlate with the ab phase transformation suggested by Roberts (1935), and Néel (1953) has considered

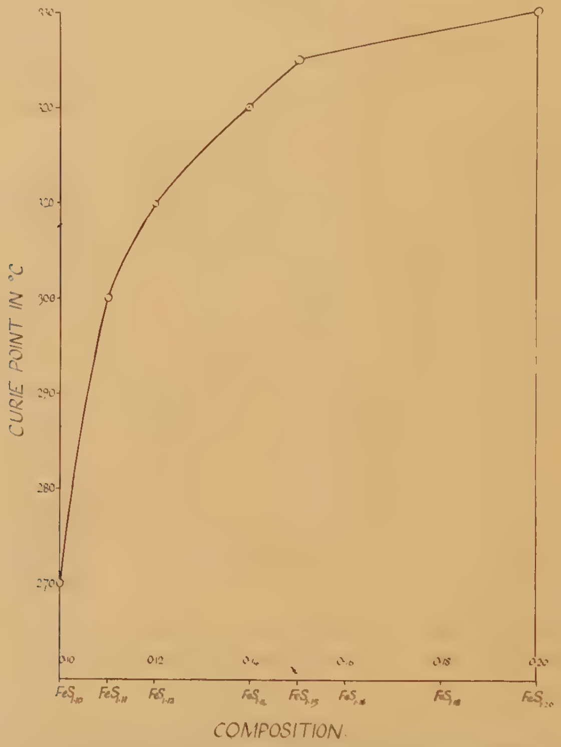
Fig. 25



Variation of specific susceptibility with temperature for sulphides of composition $FeS_{(1+x)}$ where $x > 0{\cdot}09$—data from Haraldsen (1937).

that this transformation may involve the disappearance of the ordered distribution of the vacant positions with random distribution in all iron layers above the transformation temperature. Quenching experiments by Benoit, designed to preserve the disordered arrangement of holes at temperatures below 560°C, failed to prove definitely that ordering of holes disappears at 560°C. Michel, Chaudron and Benoit (1951) report the preservation of a high temperature paramagnetic state on chilling which easily reverts to the stable ferromagnetic state.

Fig. 26



Variation of Curie Point with composition in the sulphides $FeS_{(1+x)}$ where x varies between 0·10 and 0·20.

Replacement of the excess S over the FeS ratio by Se, As, etc. has been achieved in the laboratory (Michel 1937) but is unlikely to occur in the pyrrhotite of natural rocks to any significant extent. Natural pyrrhotites may contain Ni^{++} replacing Fe^{++} but the extent of possible replacement and its effect on the magnetic properties are not known with certainty, though Ramdohr (1950, p. 404) has reported that laboratory preparations of pyrrhotite may contain up to approximately 13% Ni. At high temperatures more Ni^{++} can enter the structure than at lower temperatures so that on cooling the excess is exsolved out as lamellae of pentlandite (Fe, Ni)S.

Pyrrhotite is opaque to transmitted light and reddish brown by reflected light. It shows strong anisotropy, especially in oil, its reflection pleochroism being: o—reddish brown; e—brown, paler than o. The reflective power measured with a photometer is 36–37% in air, 28–29% under oil; or with a photocell 33·1–37·0% in air, 18·8–24·9% under oil (Ramdohr 1950). Pyrrhotite is attacked by hydrochloric acid and is said to be slowly stained light brown with nitric acid (Short 1948, p. 146). The density of pyrrhotite ranges between 4·58 and 4·65 although the calculated density for $FeS_{1\cdot 11}$ is 4·69 (Palache, Berman and Frondel 1944, p. 233).

§ 6. IGNEOUS ROCKS AND THEIR FERRIMAGNETIC MINERALS

Igneous rocks have solidified from a mutual solution of silicates, oxides and various volatile constituents (magma). Variations in the chemical composition of magmas and in the physical conditions under which solidification has taken place result in wide variation in this kind of rocks. For the present study it is convenient to recognize three groups based on chemical composition:

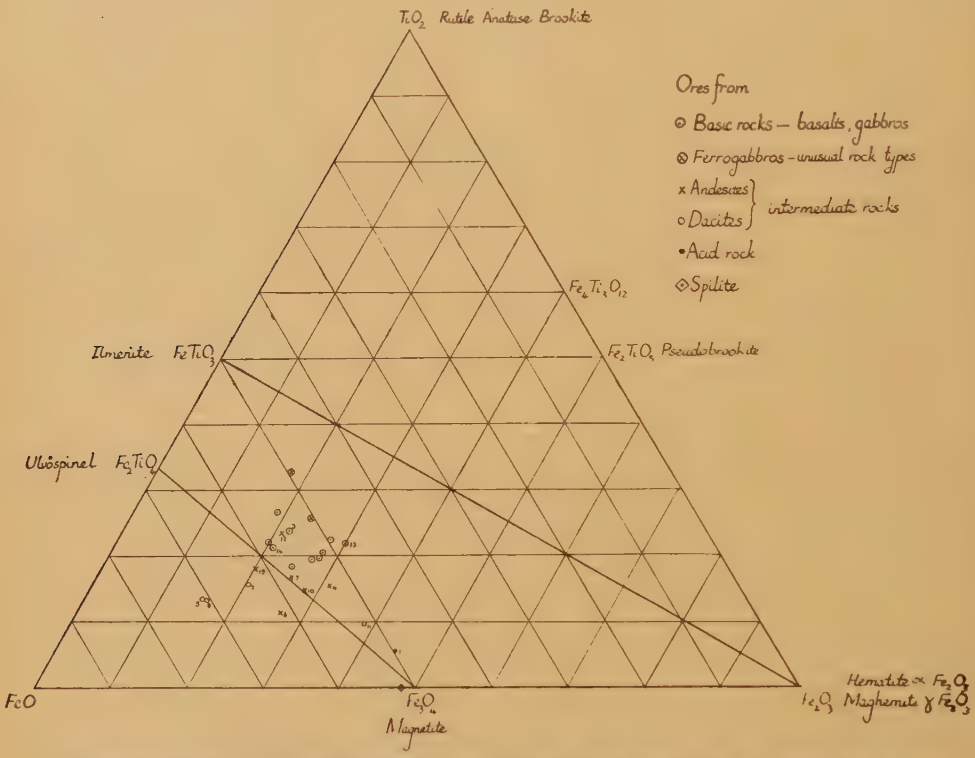
1. Acid, $SiO_2\% > 65$, including granite, rhyolite, granodiorite, dacite, etc.
2. Intermediate, $SiO_2\% < 65$ and > 52, including syenite, trachyte, many diorites and andesites.
3. Basic, $SiO_2\% < 52$, including gabbros, basalts, dolerites and related rocks.

A fourth group (the Alkaline group) including nepheline syenites, phonolites, tephrites, etc., is sometimes recognized but is quantitatively unimportant.

Crystallization may proceed in a magma still retained within the outer layers of the earth's crust or upon extrusion at the surface as a lava flow. Slow crystallization at depth results in a coarse-grained rock (plutonic). Under such conditions the volatile constituents are retained until a late stage of crystallization and their presence may extend the temperature range of crystallization. Rapid cooling and loss of volatiles usually accompanies extrusion of the magma at the surface so that the resulting volcanic rocks are characteristically fine-grained. If any crystals have begun to form in the magma before extrusion they may have dimensions much greater than those of the crystals forming after extrusion. They are termed phenocrysts (the rock is said to be porphyritic). An intermediate group of igneous rocks in which cooling proceeded at an intermediate rate (the hypabyssals), while transitional between the two extremes, includes many rocks the characters of which permit a fuller understanding of the mineralogical relationships in the volcanics and plutonics.

The compositions of the ore minerals found in igneous rocks depend on the chemical composition of the parent magma and on the physical conditions operative during their crystallization. Among the latter the rate of cooling is the principal factor in determining whether exsolution occurs and thus whether solid solutions are preserved or not. Analyses of ferrimagnetic iron oxide minerals collected from the literature and plotted in fig. 27 show the tendency for the oxide ores of basic rocks to be richer in Ti than those of the intermediates. Very few analyses of oxide ores from acid rocks are available but such as exist are still poorer in Ti. The analysis of an ore from a spilite appears anomalous in that this type of lava is often considered to be a modified basalt but until the origins of spilitic lavas are better known there are reasonable grounds for questioning whether such lavas should be included in the basic group. Apart from this anomaly there appears to be a general correlation between the composition of the oxide ore minerals and the igneous rocks in which they occur. The survey of the distribution of opaque oxides and sulphides in

Fig. 27



The composition of ferrimagnetic iron oxide minerals from igneous rocks, excluding the rare ferrimagnetic rhombohedral minerals. The numbered points refer to ores studied by Akimoto (1951 and 1954) the magnetic properties of which are listed in table 6. A general tendency for the ores of basic rocks to be richer in titanium than those of intermediate and acid rocks is apparent. Except for the two ores from ferrogabbros (rocks abnormally rich in iron) the compositions of these natural ores fall outside the 'area of immiscibility' delineated by the 1150°c contour of fig. 13.

common igneous rocks reported by Newhouse (1936) displays the same tendency. Of 31 granites examined ilmenite occurred either as discreet grains or as a component of intergrowths in only 17 and in no case unaccompanied by magnetite. Of 15 syenites 8 carried ilmenite with magnetite present in every case, but 12 out of 16 diorites carried ilmenite 3 of them without magnetite. Of 29 gabbros all the 23 which carried opaque oxides contained ilmenite and in 6 of them ilmenite occurred alone. On the other hand Baker (1952) found, on examining 6 New Guinea gabbros, that crystals of magnetite or magnetite–ilmenite intergrowths predominated and did not report free ilmenite.

The effect of conditions of consolidation on the nature of the ore fraction is illustrated by Newhouse's results for gabbros (plutonic). dolerites (hypabyssal) and basalts (volcanic). Of 17 basalts examined 9 contained magnetite alone (probably spinel solid solutions intermediate between Fe_3O_4. Fe_2TiO_4 and $FeTiO_3$), 2 contained ilmenite alone, 1 an association of magnetite and ilmenite and 4 magnetite–ilmenite intergrowths. 36 dolerites were examined and magnetite alone was recognized in only 5 ; 3 contained ilmenite alone, but magnetite–ilmenite intergrowths were recognized in 28 out of the 36 dolerites, associated with discreet ilmenite in 18 cases. No specimen of gabbro examined contained magnetite alone, but 6 out of the 29 contained only ilmenite. Magnetite–ilmenite intergrowths were recognized in 17 out of the 23 ore-bearing gabbros and were associated with ilmenite in 16 out of these 17 cases. 23% of the basalts contain intergrowths, 78% of the dolerites and 74% of the gabbros. Conversely 53% of the basalts contain spinellid ore minerals alone, 13% of the dolerites and 0% of the gabbros. Although the sampling is inadequate for definite conclusions to be drawn the suggestion that the spinel solid solutions intermediate between Fe_3O_4, Fe_2TiO_4 and $FeTiO_3$ are more likely to be preserved under volcanic conditions of crystallization is strong. Ramdohr (1950) states that unexsolved titanomagnetites are common in volcanic rocks and Ödman (1932) reports that the optical properties of magnetites in the lavas from Mt. Elgon, British East Africa are typical of magnetites containing $FeTiO_3$ in solid solution.

Natural magnetites may contain very fine exsolved bodies of aluminous spinels (Ramdohr 1950, p. 664) indicating that the amount of Al^{+++} which can be tolerated in the magnetite structure falls with decreasing temperature. A zonal distribution of such exsolved spinel indicates that the early crystallized ' magnetite ' usually contained more Al^{+++} than the later. Such exsolution intergrowths make it probable that the unexsolved spinel ores of volcanic rocks may contain more Al^{+++}, Mg^{++} etc. than the spinel ores of plutonic rocks. Where exsolution bodies of ilmenite and spinel both occur it is customary to find that the former are the older.

Oxidation of ' magnetite ' to maghemite is common in some lavas, e.g. Elgon lavas (Ödman 1932, p. 296), and has been described by Nieland from the plateau basalts of West Greenland (Nieland 1931). Maghemite has also been reported from the gabbro at Kamaisi, N.E. Japan (Nagata and

Watanabe 1950). More frequently magnetite is oxidized to hematite (often then termed 'martite' and the process 'martitization'), the hematite sometimes having a lamellar form either parallel to the octahedral faces of the host magnetite or to the growth zones of the latter. Martite intergrowths are distinguished from rare magnetite–hematite exsolution intergrowths by a concentration of the hematite marginally and along cracks in the former (Edwards 1947, Baker 1952, p. 574) compared with its even distribution in the latter. Martitization may be achieved by heated aqueous late magmatic (hydrothermal) liquors circulating through the rock, by atmospheric oxidation at or near the surface of lava flows during the initial cooling, and occasionally by strong atmospheric weathering. The conditions determining the oxidation of magnetite to maghemite are not so well known. In the Elgon lavas maghemitization is associated with extensive hydrothermal changes but Ödman (*op. cit.*) found it impossible to decide whether the formation of maghemite was brought about by the activity of the hydrothermal liquors or strong atmospheric weathering. Even less clear are the factors determining which of the two forms of Fe_2O_3 will result from the oxidation of magnetite under any specified conditions, although the instability of maghemite at even moderate temperatures suggests that oxidation of magnetite at temperatures greater than 300–400°C would yield hematite rather than this mineral.

Ilmenite–hematite intergrowths occur in plutonic rocks but in rapidly chilled volcanic rocks rhombohedral solid solutions intermediate between $FeTiO_3$ and Fe_2O_3 may persist unexsolved.

Pyrrhotite occurred in 21 of the 29 gabbros examined by Newhouse (1936), in 12 out of 16 diorites, in 8 out of 15 syenites and in none of the 31 granites. Pyrites (FeS_2) was found in 18 of the 29 gabbros, in only 5 of the 16 diorites, 5 of the 15 syenites, but in 22 out of the 31 granites. These figures suggest that the sulphide mineral of acid rocks is pyrites, not the ferrimagnetic pyrrhotite. Pentlandite (FeNiS) may be present as small exsolution lamellae in the pyrrhotite of gabbros. Newhouse reported pyrrhotite in 19 out of 36 dolerites and in 5 out of 17 basalts and pyrites in 19 of the dolerites and only 2 of the basalts. As might be expected since sulphur may escape from the lava with volcanic gases primary sulphides are less frequent in volcanic rocks than in the plutonics. Pentlandite is occasionally seen as exsolution lamellae in the pyrrhotite of dolerites but was not reported in the basalts of Newhouse. Rocks which have been subjected to hydrothermal action frequently contain pyrites and certain types of lava, e.g. andesites, are especially prone to changes during which secondary pyrites is formed.

The amounts of opaque minerals found in igneous rocks vary considerably even between specimens of the same rock type, e.g. gabbros and sometimes between specimens collected from the same rock mass. Basic rocks in general contain more opaque minerals than acid :—gabbros carry up to 10–15% of the oxide minerals ; granites rarely more than 1–2%. Sulphides rarely comprise more than 1–2% of any igneous rock (excluding secondary sulphides) and in granites rarely exceed a few tenths of 1%. These figures refer to rocks of normal characters; specimens abnormally rich in ore may contain more, e.g. 40% in ore-rich bands of certain layered gabbros and in some cases layers in this type of intrusion may be almost entirely composed of ore minerals. But such rocks are exceptional.

The grain size of the ferrimagnetic minerals also depends on the rate of cooling. In volcanic rocks the dimensions of phenocrystal ores may vary up to 0·5 mm (cf. Nagata 1953 a, p. 40) and those of the ores in the matrix from a few μ up to 0·05 mm though it is difficult to lay down limits for such a continuously varying property. In plutonic rocks wide variation is again found, crystals up to 1 mm or more in diameter sometimes being present in gabbros. In the intergrown grains the component lamellae may vary down to the limit of visibility ($\frac{1}{2}\mu$—Ramdohr 1953, p. 678) and possibly to still smaller dimensions.

The spinellid ore minerals tend to form equidimensional grains often irregular in shape but sometimes having habits based on the octahedron. The rhombohedral oxide ore minerals are usually platy so that the two types of oxide ore minerals tend to approach the two extremes of shape anisotropy.

Attempts have been made to find a relation between the Curie Point of igneous rocks and their chemical composition (Chevallier and Pierre 1932, Nagata and Akimoto 1950). The difficulty of predicting the composition of the oxide ore fraction from the chemical analysis of a rock has already been referred to, but even if this can be done with some degree of certainty the exact compositions of the ore minerals actually present will further depend on the extent to which exsolution has proceeded during the cooling of the rock. The Curie Point of the rock (the Curie Point(s) of its contained ferrimagnetic mineral(s)) will be very different if the ore minerals are present in the form of a single solid solution phase of the $Fe_3O_4 . Fe_2TiO_4 . FeTiO_3$ system than if exsolution has resulted in the formation of an intergrowth of an Fe_3O_4-rich spinel and an $FeTiO_3$-rich rhombohedral mineral even though chemical composition may be identical in the two cases. Being dependent on the actual composition of the ore minerals present and not on their amounts, Curie Point should not be expected to show any close relationship to chemical composition of the rock as a whole.

The temperatures at which magmas crystallize are usually well above the Curie Points of the natural ferrimagnetic minerals. Magmatic temperatures may be estimated by observation of lava temperatures at volcanic vents or maximum values by determinations of the temperatures of incipient melting and ready flow of rock specimens heated in the laboratory. Estimated lava temperatures vary between 1050–1200°c (Daly 1933, p. 68) and in view of Kennedy's demonstration that exothermic oxidation reactions at the surface are unlikely to raise lava temperatures by any significant amount (Kennedy 1948) these values may be taken as close estimates of magmatic temperatures. The temperature of incipient melting in basalts appears to be close to 1050° for several specimens examined although the well-known Palisades dolerite does not begin to fuse until heated to 1150°c but flows readily at 1225°c (Daly, *op. cit.*, p. 66). Various andesites begin to fuse at approximately 1100° and flow freely at only slightly higher temperatures. Granite begins to melt at below 700°c (probably at 570°) and if held for a week at 800°c becomes half molten (Daly, *op. cit.*). This satisfactory agreement between the two methods of estimation further accords with the findings of Hess (1941, pp. 582–4), who, basing his estimates on phase transformations in the pyroxene group of minerals, concluded that certain basic rocks (gabbros) crystallized over a temperature range *ca.* 1140–950°c. The rocks in question are plutonics and the temperature range of crystallization may be rather more extensive than would be the case with volcanics of the same basic composition. The vast amount of experimental data accumulated by N. L. Bowen and his associates at the Geophysical Laboratory, Washington, clearly indicates that granites would crystallize at somewhat lower temperatures and possibly over a more extended range.

The period of crystallization of the opaque oxide minerals differs in different rock types. In basic rocks they have frequently crystallized during and after the main period of silicate crystallization, in intermediates slightly earlier than and during the main silicate period and in acids earlier than most silicates (Newhouse 1936, Baker 1952). Similar relationships obtain for the sulphides, complicated in some basic rocks by the separation of an immiscible liquid sulphide phase during cooling which solidified later than the silicate liquor. It is, however, probable that the temperature range of formation of naturally occurring ferrimagnetic oxides is not very different from 1100–800°c (the lowering of the liquidus surface for the $FeO . Fe_2O_3 . TiO_2$ system by the presence of silicates must be marked).

The extent of exsolution taking place depends on the rate of cooling of the oxide minerals after their crystallization and particularly through the exsolution temperature range. Cooling is generally slower under plutonic conditions but the rate of cooling is not uniform. While the bulk of the silicates are crystallizing the liberated latent heat of crystallization offsets the cooling by heat loss to the environment and the temperature of the crystallizing magma falls slowly. When crystallization is complete the temperature tends to fall more rapidly at first, but as the igneous rock and its environment attain similar temperatures the rate of cooling of the igneous rock slackens off again. This last stage is quickly reached in a plutonic environment and hardly achieved in a volcanic one. If the exsolution temperature of an oxide solid solution is attained during the second period of rapid cooling exsolution will be inhibited and the solid solution preserved but if it coincides with a period of slow cooling exsolution will occur. A comparison of fig. 13 showing a probable form for the solvus surface in the system $Fe_2O_3 . FeO . FeTiO_3$ and fig. 27 showing the compositions of oxide minerals from various igneous rocks, taken together with a consideration of the probable temperatures of formation of these oxide minerals indicates that in basic rocks exsolution of a rhombohedral phase from a spinel solid solution might commence during the first period of slow cooling. The temperatures for exsolution into two spinels would be attained during the third period and therefore exsolution of this sort should not be expected in volcanic rocks. Earlier, it has been suggested, to account for the relationships found in natural ores, that the field for exsolution of spinel solid solutions of the $Fe_3O_4 . Fe_2TiO_4 . FeTiO_3$ system into two spinels may be more extensive if foreign ions are present. Another explanation is just possible. The curious form of the solvus surface in this system may be due to the interaction of two 'solvus surfaces'—one for spinel-rhombohedral exsolution the other for two-spinel exsolution. In the spinel-rhombohedral intergrowth field the former is above the latter—in the two-spinel field the reverse is true. An $Fe_3O_4 . Fe_2TiO_4 . FeTiO_3$ solid solution may exsolve into a spinel-rhombohedral intergrowth during the first period of slow cooling, then during the second period of more rapid cooling failure to exsolve completely may preserve a metastable spinel phase, which during the third period of slower cooling may pass through the lower solvus surface and exsolve into two spinels. Conversely ores in the field of two-spinel exsolution might first form two spinels but subsequently exsolve a rhombohedral phase when cooled through the lower solvus after rapid cooling. The fragmentary data which does exist suggests that although the oxides of some intermediate rocks behave like those of basic rocks the oxides of others pass through their exsolution temperatures during the period of more rapid cooling. As pointed out earlier there is too little data on the ores of acid rocks for any general conclusions to be drawn.

Thermoremanent magnetization of igneous rocks develops when their contained ferrimagnetic minerals cool through their Curie Point temperatures. From the foregoing we may generalize that in volcanic rocks crystallization and exsolution will be complete at temperatures well in excess of Curie Point temperatures but that in plutonic rocks exsolution may still have been proceeding slowly at temperatures comparable to the Curie Point of the ferrimagnetic oxides.

Changes of Curie Point on heating cubic oxide ore minerals have been reported by Akimoto (1951) who, in his studies on the thermal change of magnetic susceptibility of these minerals, reported four types of change :—

(*a*) high-susceptibility and reversible type,
(*b*) high-susceptibility and irreversible type,
(*c*) low-susceptibility and reversible type,
(*d*) low-susceptibility and irreversible type.

The two irreversible types are marked by a change of Curie Point. In the reversible type the variation in susceptibility with temperature during heating gives the same curve as that obtained during cooling. In the irreversible type the cooling curve is not coincident with the initial heating one but on subsequent heating and cooling the initial 'cooling' curve is followed. It thus appears to represent a more stable condition. Subsequently Akimoto (1954) showed that similar reversible and irreversible behaviour may be observed in the variation of spontaneous magnetization with temperature. He demonstrated a change in the cell dimensions for those minerals of irreversible behaviour, which in all cases except two involved a slight increase in the value of the dimension *a* and a fall in Curie Point which ranged from 40° to 140°C. In his later, more detailed work he showed that after heating two Curie Points could be recognized in some cases, one equal to or above the original and one below, and inferred that the decrease of Curie Point is caused by an increase of the content of Fe_2TiO_4 in an $Fe_2TiO_4 . Fe_3O_4$ specimen owing to heat treatment up to about 600°C. That the changes in the magnetic behaviour result from some phase changes in the material is probably true and where two Curie Points are observed after heating the suggestion of some form of exsolution is strong, but a plot of Akimoto's data on a $Fe_2O_3 . FeO . FeTiO_3$ diagram (fig. 27 and table 6) shows little obvious relationship between composition

Table 6. Cell Dimensions and Magnetic Properties of Cubic Iron-Titanium Oxide Minerals (data from Akimoto 1954), the compositions of which are plotted in fig. 27

	Cell dimension *a* in Å		Curie Point °C		Intensity of saturation magnetization at room temperature
	H	*C*	*H*	*C*	
1	8·419	—	500	—	80 e.m.u./g
2	8·419	—	490	—	90
3	8·453	8·456	440	300	44
4	8·422	8·426	505	505, 410	66
5	8·442	8·447	480	500, 390	75
6	8·449	8·447	500	510, 410	65
7	8·426	8·432	380	435, 360	59
8	8·436	8·439	490	500, 440–380	67
9	8·420	8·427	510	510, 380	66
10	8·424	8·432	500	410	61
11	8·414		480	455	79
12	8·445		530	530	48
13	8·41 8·44		560	555	28
14	8·459	8·451	490	400	31
15	8·447	8·450	510	530	54

No chemical data for 9 : therefore not plotted on fig. 27.
Cell dimension *a* : *H*—value determined before heating.
C—value determined after heating and subsequent cooling.
Curie Point *H*—Curie Point determined on heating.
C—Curie Point determined during cooling after heating.

as reported and Curie Point, either before or after heating, or the intensity of magnetization at room temperature. This may be due to the presence of foreign ions in the ore minerals not reported in the analyses or it may indicate that some of the ores were already finely exsolved intergrowths before examination so that the bulk composition as reported does not correspond to the composition of either component. The change in Curie Point in those cases where two Curie Points are observed after heating accords with a two-spinel exsolution better than with a spinel-rhombohedral exsolution and supports the earlier-expressed view that in natural ores the field for exsolution into two spinels at temperatures of the order of 600° is perhaps more extensive than the experimental data might lead us to suppose. With further data it may eventually be possible to decide whether this is exsolution of metastable spinel phases on heating up to the hypothetical ' lower solvus ' or not. Such an explanation might apply for specimens 4–10 examined by Akimoto (table 6). If, however, the irreversible behaviour is due to some process of homogenization or exsolution the reversible behaviour may be shown only by specimens which can be neither homogenized or made to exsolve further on heating to 600°c. This could be due to exsolution having already proceeded to the limit possible or to the solid solution being stable at temperatures of 600°c and below. No. 2 of Akimoto's specimens could represent the former; nos. 1, 12 and 13 the latter. In his earlier paper Akimoto (1951) correlated the high-susceptibility reversible types with slow cooling from a low temperature, the low-susceptibility types with rapid cooling from a high temperature and the high-susceptibility irreversible types with intermediate conditions. The low susceptibility minerals may therefore represent metastable spinel phases preserved through chilling which may or may not undergo exsolution on reheating to 600°, dependent on whether their compositions are such that they lie in the two-spinel exsolution field and therefore pass through the lower solvus on such heating. Unfortunately too little data is available yet to map limits for this exsolution field and at present it is difficult to predict whether exsolution may be expected on heating up to 600°c or not.

§ 7. Sedimentary Rocks and their Ferrimagnetic Minerals

Almost all sedimentary rocks formed at temperatures considerably below the Curie Points of the ferrimagnetic minerals they contain. The exceptions are the pyroclastic rocks, i.e., volcanic ashes and their consolidated equivalents the tuffs, which represent finely comminuted igneous material explosively erupted from a vent during volcanic activity. The sandstones, shales and limestones, the three end members of the variation in sedimentary composition, all accumulated at lower temperatures. The material accumulating as sediments was originally derived by the breakdown, either mechanical or chemical, of pre-existing rocks and has been transported to the area of accumulation (deposition) by one of the natural transporting agents (wind, moving water or ice). Further breakdown may take place during transportation at any stage and three main groups of breakdown products may be recognized:

(1) Material derived from the pre-existing rocks by simple mechanical disintegration, e.g., small rock fragments, quartz, white mica.

(2) Material resulting from the chemical breakdown of the pre-existing rocks and occurring in the form of extremely finely divided crystals, e.g. the clay minerals, kaolinite, illite, etc.

(3) Material resulting from the chemical breakdown of the pre-existing rocks but transported in solution—only possible of course if the transporting agent is water. The proportions of the three groups depend on the conditions under which the pre-existing rocks are broken down. Under conditions adverse to chemical attack, i.e. glacial conditions on the one hand, arid conditions on the other, most of the material will be of the first group. Under optimum conditions for chemical attack, i.e. warm humid climatic conditions most of the material will be of groups 2 and 3.

Generally speaking the first group on deposition forms sandstones and associated rocks, the second the clays, shales and allied argillaceous sediments, and the third the limestones (either by direct precipitation or through the intervention of organic agencies) and such formations as rock salt beds. Exceptionally, when the bulk of the material is derived by mechanical disintegration of rocks and especially when it has been further ground down by transportation in ice, material of the first group may give rise to 'clays'—the glacial varve clays—which have few mineralogical affinities with the argillaceous sediments. Mineralogically they are probably closer to the sandstones but are much finer grained.

The behaviour of iron during the breakdown of the pre-existing rocks and its subsequent transportation and deposition depends on a number of factors. Magnetite, ilmenite and hematite (especially the latter) are fairly resistant to chemical weathering (and thus enter group 1) but ferrous-iron-containing silicates are often easily attacked liberating ferrous ions generally into solution (group 3). Further oxidation of Fe^{++} to Fe^{+++} with resulting increase of ionic potential leads to hydrolytic precipitation of ferric hydroxides (group 2). Goldschmidt (1954) suggests two rules governing the fixation and mobilization of iron viz.

(i) Oxidizing conditions promote the precipitation of iron, reducing conditions promote its solution.

(ii) Acid conditions (low pH) generally promote solution of iron, alkaline conditions (high pH) promote its precipitation. Ferric hydroxide is easily precipitated from aqueous solutions of pH3, ferrous hydroxide is first precipitated at *ca.* pH7.

When considering marine sediments it is convenient to recall that the pH of sea water is about 8 so that the solubility of Fe^{+++} in sea water is extremely low and the bulk of the iron which enters the sea is precipitated as ferric hydroxide provided that oxidizing conditions are present. This oxidative precipitation of iron may occur in shallow lacustrine and brackish as well as aerated marine waters. In many cases the precipitation of ferric hydroxide coincides or at least overlaps the sedimentation of the aluminous muds and the clay minerals so that argillaceous sediments may contain significant quantities of precipitated ferric hydroxide. Equally well ferric hydroxide may be precipitated along with the first group of sedimentary materials so that the rocks resulting from the accumulation of this material may contain iron minerals of detrital origin (magnetite, ilmenite, hematite etc.) and also derivatives of the precipitated ferric hydroxide (which ages into goethite αFeO(OH), or possibly but much more rarely lepidocrocite γFeO(OH)). Limestones etc. will contain very little iron and will have very slight magnetization, if any. For the present purpose it will be convenient to distinguish three types of sediments carrying iron oxide minerals :—

(*a*) Those which carry only mechanically derived iron oxides, e.g. varve clays, certain sandstones.

(*b*) Those which carry both mechanically derived iron oxides and chemically precipitated ferric hydroxide or its derivatives, e.g. certain sandstones, silts and marls.

(*c*) Those which carry only chemically precipitated iron oxides, e.g. certain shales.

The chemically precipitated ferric hydroxide may suffer dehydration either during compaction of the sediment or later and gives rise to the corresponding form of Fe_2O_3 (hematite from goethite, maghemite from lepidocrocite). The ferric oxide mineral is extremely finely divided often beyond the limit of visibility under the microscope. Appreciable line broadening obtained on x-ray powder photographs shows that the αFe_2O_3 obtained by dehydrating synthetic goethite (Rooksby, in Brindley 1951) is of a grain size probably well below $0{\cdot}1\,\mu$. Such dehydration probably proceeds in natural rocks at quite low temperatures and any remanent magnetization in the resulting ferric oxide mineral will be essentially an isothermal remanent magnetization and probably unstable (Nagata 1953 a, p. 109). The detrital iron oxide minerals may have a grain size 100–1000 times greater than that of the oxides arising by dehydration, except in varve clays where detrital magnetite particles range in diameter from $0{\cdot}01\,\mu$ to $5\,\mu$ with most of them in the range $0{\cdot}1\,\mu$–$0{\cdot}5\,\mu$ (Graham 1949, p. 143). These particles may be considered to be minute magnets at the time of deposition and with freedom of movement will tend to be aligned relative to the earth's field. Their magnetization will have been acquired at an earlier stage in their history, probably in the pre-existing rock from which they were derived. If this was igneous their magnetization will have the stability of a thermo-remanent magnetization.

Those sedimentary rocks the remanent magnetization of which is due largely or entirely to detrital ferrimagnetic oxides would be expected to be stable magnetically and this seems to be the case (compare Johnson, Murphy and Torreson 1948, Graham 1949—type (*a*) of the above grouping, etc.). In those rocks carrying both detrital iron oxide minerals and iron oxides of precipitated origin (type (*b*)) the stability of the remanent magnetization may depend on the contribution made to it by the magnetizations of the two types of oxide mineral. In their studies of a series of red sandstones and marls containing black detrital grains of hematite and a red hematite cement (probably precipitated origin) Creer, Irving and Runcorn (1954) found that their specimens could be grouped into those which were entirely stable in the earth's field, those which were partially stable and those which were completely unstable. They attributed this to variation in the relative proportions of the two sorts of hematite. Clegg, Almond and Stubbs (1954) in their studies of the magnetism of red sandstones of Triassic age similarly found evidence of two magnetic components in their rocks.

The extent to which the magnetic polarizations of sedimentary rocks witness the orientation of the earth's field at the time of their formation depends on several factors among which the degree to which the detrital ferrimagnetic minerals are aligned with their own magnetic polarizations in direction of the field is important. Laboratory experiments on the deposition of sediments in still water in a controlled field have been carried out by several investigators (Johnson, Murphy and Torreson 1948, Nagata, Rikitake and Akasi 1943 ; Lloyd reported in Clegg, Almond and Stubbs 1954). The horizontal direction of magnetic polarization of the artificial deposits coincides with the horizontal magnetic force but the dip is usually less than that of the applied field. The difference may amount to 20° for weak fields but decreases progressively as field strength increases. Nagata (1953 a, p. 198) tentatively suggests that this may be associated with a tendency for small grains of magnetite to aggregate into chains but does not give any precise indication of how this could lead to the observed effect. The shape of the particles determines the extent to which they will tend to be orientated by gravitational and hydrodynamic forces during settling, and in weak fields such forces may exert an effect comparable to the magnetic one. Magnetite particles are often nearly equidimensional, but may be flattened parallel to the octahedral faces either by crystal distortion due to twinning, fracture of a grain along the octahedral parting or break-up of magnetite–ilmenite intergrowths. The flattened particles would have their direction of easiest magnetization either perpendicular to their large faces or making an angle of 18° with it (i.e. along a triad axis). The two extreme conditions of settling (i) under no effect of gravitational and hydrodynamic forces and (ii) under no effect of magnetic forces give rise to magnetic polarizations of the resultant aggregates which are parallel to the ambient field in dip in the former case and horizontal in the latter where the flakes settle with their long axes horizontal, but either way up (assuming in both cases no re-orientation after settling). The relative effect of gravitational and hydrodynamic forces on the one hand and magnetic forces on the other will determine the final direction of polarization due to these platy grains. For the whole rock it will be subject to modification by the polarizations of grain groups of different relative proportions with, in the extreme case, spherical grains always being aligned with their axes of polarization parallel to the dip of the ambient field. The only conclusion that may be safely drawn appears to be that the dip of the magnetic polarization of a sedimentary rock is an unreliable indicator of the dip of the earth's field at the time the rock was formed. Occasionally the polarizations measured on a series of separated specimens in one stratum show a wide scatter (Torreson, Murphy and Graham 1949, p. 128, Graham 1949, p. 146) which has been attributed to disturbed conditions of deposition. Some support for this view is afforded by the observations of King (reported in Griffiths 1954) that currents of a few centimetres per second in the water have quite large effects on the magnetization direction of redeposited varves. King has also shown that if deposition takes place on a sloping surface the effect is roughly the same as if deposition has occurred on a horizontal surface and this had subsequently been tilted.

Changes of a chemical and physical nature—diagenetic changes—commence in the sediments very soon after deposition and in some cases continue until most of the rock has been entirely reconstituted. They range from the expulsion of water from muds to form clays to the extreme cases of replacement of limestone by hematite and quartzite by pyrites. Since obviously altered rocks are usually avoided in rock magnetism studies only the minor changes will be discussed here.

When first deposited muds may contain up to 70–90% water, but with compaction by settling and under the weight of accumulating overlying sediment the water may be expelled until under a few thousand feet of overburden it may only make up 30–35% of the clay. Clegg, Almond and Stubbs (1954) report that in laboratory tests a magnetization of comparable intensity to the parent rock could be induced in redeposited rock powder provided that the water content is greater than 50%. It appears likely then that the field finally determining the polarization of the magnetization of a stable argillaceous sediment will be that operating some time after the first accumulation of the sediment. General estimates of the time lapse involved can hardly be made—each case would require individual treatment—but it may be said that anomalous polarization directions obtained from magnetically stable argillaceous rocks could be due to this time lapse in the stabilization of the magnetic polarization on formation.

Further consolidation of a shale is by recrystallization as well as compaction. Consolidation of a sand involves some compaction but the deposition of a cement is the most important factor in the lithification of a sandstone. Ferruginous cements (hematite and an extremely fine-grained form of goethite–limonite) are common in the Old Red, New Red and Lower Cretaceous sandstones of Britain and appear to have been deposited, in part at least, after the initial formation of the sandstones. These cements, crystallizing at low temperatures, will acquire a kind of isothermal remanent magnetization in so far as they develop one at all.

With deep burial they may be heated up perhaps as much as 100°c (Clegg, Almond and Stubbs 1954) and thus acquire a thermo-remanent component which will tend to be much more stable. Older rocks, with increased possibilities of having been deeply buried or heated in connection with extensive earth movements (orogenesis) might be expected on the whole to display a greater stability of their natural remanent magnetization and this seems to be so (Creer, Irving and Runcorn 1954).

§ 8. METAMORPHIC ROCKS AND THEIR FERRIMAGNETIC MINERALS

Metamorphic rocks originate through the recrystallization of existing rocks under the influence of rising temperature, shearing stress, pressure and the chemical activity of solutions permeating the minute breaks, cracks and spaces in the rock. Two main kinds of metamorphism may be recognized for the present purposes :—

(1) Regional metamorphism—recrystallization of large areas of rock due to a regional rise in temperature, change in shearing stress etc.—giving rise to schists, gneisses and allied rocks.

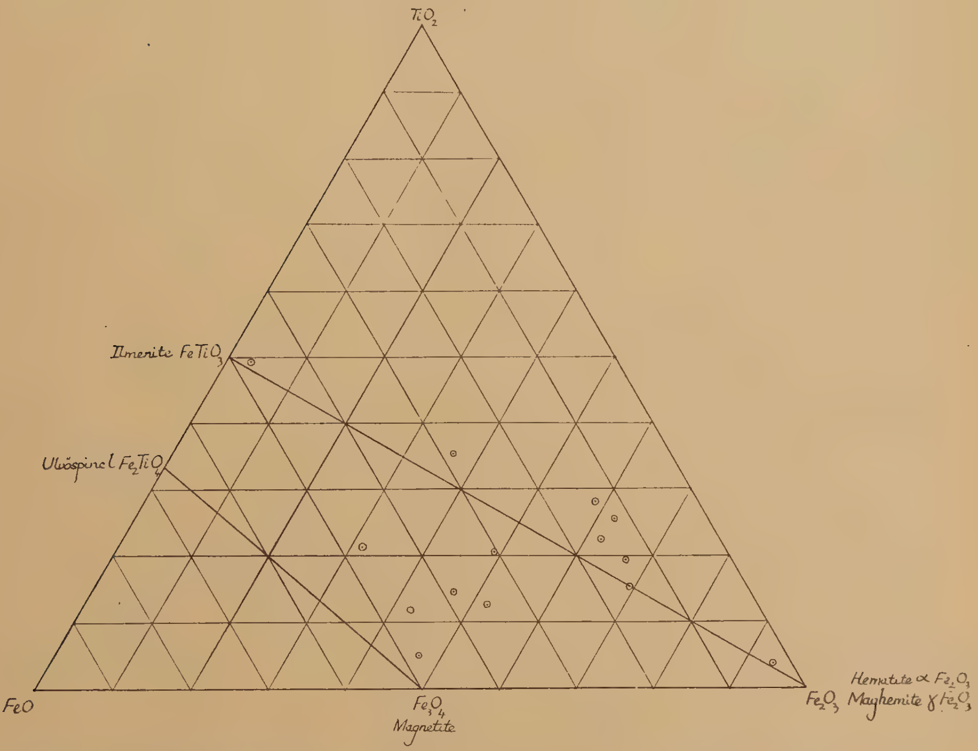
(2) Contact metamorphism—recrystallization of rocks in the immediate vicinity of an igneous intrusion due chiefly to a rise in temperature through the heating effect of an igneous magma—giving rise to hornfelses.

Data on the compositions of the iron–titanium oxide minerals of metamorphic rocks is scanty, but Balsey and Buddington (1954) have recently published a table of compositions of the oxide minerals of a series of Adirondack igneous and metamorphic rocks of Pre-Cambrian age. Their results are plotted in fig. 28, which illustrates a tendency for these ores to be richer in Fe^{+++} than is the case for the iron oxide minerals of igneous rocks. Earlier Balsey, Buddington and Fahey (1952) had reported that the major iron oxide mineral in certain gneisses from the N.W. Adirondack Mountains, New York, was ilmeno–hematite (titanium-bearing hematite with a little exsolved ilmenite) or titaniferous hematite (TiO_2 up to about 10%). Magnetite is frequently mentioned in the literature on regionally metamorphosed rocks and Harker (1939, p. 210) suggests that reduction of hematite to this mineral occurs at a very early stage but precise identifications of the nature of the ore mineral appear to have been rarely attempted. Martitized magnetite has been reported by Baker (1952) in a granulite from New Guinea and from another regionally metamorphosed rock (amphibolite) he has described magnetite–hematite exsolution intergrowths together with ilmenite.

The temperatures at which regional metamorphic changes occur have been estimated by Turner (1948, p. 285) to lie between 200°c and 800°c. Rocks subjected to quite intense regional metamorphism may easily therefore have been heated to temperatures above the Curie Points of their contained ferrimagnetic minerals so that on cooling a thermo-remanent magnetization may have developed. The magnetic polarization of such rocks will be related to the earth's field at the time of the metamorphism and not at the time of first formation of the rock.

The temperatures attained during contact metamorphism may exceed the 800°c suggested as an upper limit for regional metamorphic changes but they are unlikely to reach the 1000–1200°c suggested by Goldschmidt (1911). They will vary with the size and nature of the igneous body being highest in the vicinity of basic intrusions. That the Curie Points of ferrimagnetic minerals are sometimes exceeded is clearly demonstrated by Kato, Takagi, and Kato (1954). These authors studied a series of basaltic andesite dykes with a magnetic polarization nearly opposite to the present earth's field, cutting a green tuff (with polarization nearly parallel to the present earth's field), and found that immediately adjacent to the dykes the magnetic orientation of the tuff changes rapidly to that of the dyke. In a typical example the tuff for approximately six inches on either side of a seven foot dyke had a magnetic polarization essentially parallel to the dyke rock. It appears extremely probable that the

Fig. 28



The compositions of iron oxide minerals from Pre-Cambrian igneous and metamorphic rocks from the Adirondack Mountains, U.S.A. (after Balsey and Buddington 1954). These ores are richer in ferric iron than those from igneous rocks plotted in fig. 27, but again lie outside the 1150°c contour of fig. 13.

ferrimagnetic components of the tuff were demagnetized by metamorphic heating and subsequently acquired a new thermo-remanent magnetization on cooling.

§ 9. STABILITY OF THE FERRIMAGNETIC OXIDE MINERALS SUBSEQUENT TO THEIR INITIAL FORMATION

Normal atmospheric weathering only slowly affects the ferrimagnetic oxide minerals of rocks. They are less susceptible to such alteration than other minerals likely to occur in the same rocks so that rocks in which the ferrimagnetic minerals have been oxidized by weathering would almost certainly be rejected for rock magnetism work on account of their obviously altered condition. Magnetite is oxidized to hematite, or, rarely, maghemite. Hematite is stable. Ilmenite yields different products according to the duration and temperature of the oxidation change. Held at 520°c for 38 hours finely powdered ilmenite is partially altered to hematite and brookite, at 730°c for 4 days it yields hematite, rutile and minor brookite and at 900°c for 24 hours pseudobrookite and rutile (Basta 1953, p. 102). Anatase may also be a product of the oxidation of ilmenite and in some tropical beach sands oxidizing conditions have been sufficiently strong to cause alteration of ilmenite to hematite, rutile and anatase, the so-called ‘ arizonite ’.

Oxidation during the later stages of cooling of igneous rocks by circulating hot aqueous solutions of magmatic parentage (hydrothermal solutions) may, however, cause pronounced oxidation of magnetite etc. to hematite or, at relatively low temperatures (<300°c), maghemite. The hematite forms marginally to the magnetite grains and along cracks and the octahedral parting of the latter (martitized magnetites). Magnetite and other spinel ores, which had developed thermoremanent magnetization on cooling from higher temperatures, may suffer later oxidation to hematite (or maghemite) with consequent modification of the magnetic properties of the rock. Oxidation of this sort has been made a feature of one hypothesis to explain reversed remanent magnetization of rocks (Graham 1953). But once the rock has completely cooled down its magnetization is unlikely to undergo significant change due to weathering effects alone. Explanations of the decay of rock magnetization should be sought in physical mechanisms rather than mineralogical ones.

Heating of rocks in the laboratory in the course of thermomagnetic investigations may result in mineralogical changes modifying the magnetic properties of the rock. If this heating is carried out under conditions such that oxidation is impossible, e.g. in a nitrogenous atmosphere, these changes are limited to physical changes such as :—

1. An irreversible inversion such as the conversion of maghemite to hematite.

2. Continued exsolution of an intergrowth in which an unstable state had been preserved by chilling.

3. Homogenization, partial or complete, of an exsolution intergrowth.

4. Recrystallization of an intergrowth with consequent destruction of the intimate association of ferrimagnetics in such textures.

Graham (*op. cit.*, 249) considers the non-reversible reaction producing weakly magnetic hematite from the strongly magnetic maghemite is one of the most important physical and chemical changes (having a bearing on the magnetic properties of rocks) to occur in rocks on laboratory heating. When maghemite is present originally this will be so, but as far as is known at present maghemite is not commonly found in significant quantity in igneous rocks. Possible exsolution effects on laboratory heating have already been considered in the earlier discussion of the work of Akimoto (1951 and 1954) on ‘ reversible ’ and ‘ irreversible ’ types of ore mineral. In view of the relatively short period during which the material is maintained at an elevated temperature exsolution of a chilled phase is more likely to produce significant effects rather than stabilization of an exsolving intergrowth. Homogenization, while theoretically possible, is much less likely to produce significant effects during the short period of heating for it can only proceed during the restricted period of time when the material is above its solvus temperature. Until this temperature is attained and as soon as cooling causes the temperature to drop through this value exsolution will tend to be promoted. During a heating cycle there will therefore be two opposed effects even if the compositions of the intergrowths present are such that homogenization is theoretically possible on heating to 600–700°C. Recrystallization of an intergrowth is likewise a disturbance of a near-equilibrium condition which would be expected to require more time than that occupied by a normal heating cycle.

Thermomagnetic investigations intended to reproduce in the laboratory the original magnetic behaviour of igneous rocks when first cooled down may not do so therefore, on account of changes in the ferrimagnetic constituents, especially through exsolution effects. But the changes are likely to be of intensity rather than direction of remanent magnetization. Studies based on the polarity of rock magnetism are unlikely to be subject to error through laboratory heating of the samples.

§ 10. REVERSED NATURAL REMANENT MAGNETIZATION OF ROCKS

It is now known that there are many examples of rocks which exhibit reversed natural remanent magnetization (Mercanton 1926, 1931 and 1932, Bruckshaw and Robertson 1949, Roche 1950, 1951, Nagata 1951, Hospers 1953, Clegg, Almond and Stubbs 1954 and others). Many geophysicists consider that their existence is evidence of a periodic reversal of the earth's field (e.g. Creer, Irving and Runcorn 1954, Nagata, Akimoto, Uyeda 1954, p. 36 and many others) but mechanisms have been suggested whereby a rock can become magnetized in a direction opposed to the field in which it acquires its magnetization. Néel (1951) has proposed four theoretical possibilities viz :—

1. The rock may contain a mineral having the specific property of

developing a thermo-remanent magnetization reversed to the field in which it cools, such as the Li–Fe–Cr spinel synthesized by Gorter and Schulkes (1953).

2. The rock may have originally contained a ferrimagnetic mineral which subsequently suffered chemical change, the effect of which was to decrease or destroy the partial magnetization in the direction of the earth's field leaving the partial magnetization reversed to the earth's field dominant.

3. The rock may contain aggregates of two finely divided ferrimagnetics of different Curie Points which were in existence when the rock cooled through the higher Curie Point. The ferrimagnetic of higher Curie Point (*A*) would be magnetized parallel to the external field; that of lower Curie Point (*B*) would then be magnetized in a field which would be the resultant of the external field and the demagnetizing field of *A*, which according to the hypothesis may be in a direction opposed to the external field. In certain circumstances the development of thermo-remanent magnetization in *B* may so proceed that its effect outweighs that of *A* at ordinary temperatures and the resultant thermo-remanent magnetization of the rock would be reversed to the field in which it developed.

4. The rock may have originally contained similar aggregates to those just mentioned but may have suffered chemical alteration involving the destruction (complete or partial) of *A* subsequent to the magnetization of *B*. This hypothesis could apply even if the thermo-remanent magnetization of *B* never outweighed that of *A* before alteration.

Graham (1953) has suggested that partial oxidation of the magnetite of magnetite–ilmenite intergrowths to maghemite, with magnetization of the latter in the demagnetizing field of the former and subsequent easier demagnetization of the residual magnetite on account of its larger grain size, could lead to a reversed remanent magnetization.

If the first or third of Néel's hypotheses were applicable to a particular rock it would be expected to acquire a thermo-remanent magnetization reversed to the external field on laboratory cooling from temperatures above the Curie Points of its contained ferrimagnetic minerals. A few rocks having reversed remanent magnetization do so (Nagata 1951, Balsey and Buddington 1954, p. 26–27). Most do not. No natural ferrimagnetic mineral having the self-reversing property of Néel's first hypothesis has yet been reported. But associations of two ferrimagnetics, as required by the third hypothesis, have been reported in the self-reversing Haruna dacite lava examined by Nagata and his colleagues (Nagata, *op. cit.* and 1953 b, Nagata, Uyeda and Akimoto 1952, Nagata, Uyeda, Akimoto and Kawai 1952, Nagata, Akimoto and Uyeda 1953), and the reversed remanent magnetization of certain Adirondack rocks has been interpreted as the result of the action of the normal earth's field on the inherent properties of the grains of intimately mixed hematite and ilmenite which they contain (Balsey and Buddington 1954, p. 26).

In the Haruna rock, a highly vesicular acid volcanic lava, Nagata and his co-workers found a ferrimagnetic spinel mineral of Curie Point about

500°c (A), a ferrimagnetic rhombohedral mineral of Curie Point about 230°c (B) and 'mixed' grains containing both A and B. Examination of the thermo-remanent magnetization of single grains led them to conclude that each grain of the A constituent with a Curie Point in the range 430–510°c has weak normal T.R.M.* and each grain of B with a Curie Point 230–240°c also has weak normal T.R.M. But the AB grains have strong reversed T.R.M. On the basis of a thermo-magnetic separation Nagata, Akimoto and Uyeda (1953) further recognized AB grains in which $m_B/m_A < 20$ (where m_B is the mass of B, m_A the mass of A) and AB grains in which $m_B/m_A > 30$ and deduced a moderate or weak reverse T.R.M. for the former (Ab grains) and a strong reverse T.R.M. for the latter (aB grains). Of 106 grains examined, 67 were of A, 22 Ab, 15 aB and 2 of B. If the sum of the reverse magnetization of these AB grains exceeds that of the normal magnetization of the A and B grains the rock as a whole will show reverse T.R.M. It would appear that the grains examined must have varied considerably in size for the chemical data on the ore minerals of the Haruna rock indicates that the ratio of the amount of A to that of B is approximately 100 : 1. A still unsolved problem of the Haruna dacite is how the increase in the magnetization of B with decreasing temperature can overcome the normal magnetization of A when the latter is nearly 100 times more abundant, for the reversed magnetization of the B constituent of the AB grains must overcome not only the normal magnetization of the A in the AB grains but also that of the discreet A grains before the rock as a whole will show reversed remanent magnetization. Another concerns the detailed mechanism of the assumed magnetic coupling between the A and B phases of the AB grains which may be on a domain scale (Nagata, Uyeda and Akimoto 1952). B has been said to occur in thin bands (Nagata, Akimoto and Uyeda 1953, p. 183) sometimes intergrown with the A phase, but examination of polished sections in reflected light fails to reveal any regular intergrowth such as might be expected to have a physical significance. It is difficult to escape the conclusion that self-reversal in the Japanese rock is due not only to the presence of an intergrowth of ferrimagnetics along the lines of Néel's third hypothesis but also to unusual properties of one or other (or both) of the ferrimagnetics. The saturation magnetization of B at 0°c is about 20 e.m.u./g (Nagata, Akimoto and Uyeda, *op. cit.*, p. 181) and it is thus quite strongly ferrimagnetic. The nature and possible origin of such ferrimagnetic rhombohedral ores has been discussed earlier (p. 150) where it has been suggested that they represent metastable states preserved only by chilling. Rapid chilling certainly affected the Haruna lava subsequent to an earlier period of slow cooling and crystallization of hornblende, hypersthene, plagioclase and the ore minerals, for the remainder of the rock is a highly vesicular glass. Phillips (1954), after etching with HF a polished section of the reversing fraction of the ore minerals of this rock, reported a complex micro-structure in the grains—innumerable square crystallites 1–2 μ in diameter set in a finely granular matrix containing a good deal of yellow sulphide of rectangular form $\frac{1}{4}$–$\frac{1}{2}$ μ wide and $\frac{3}{4}$–2 μ long in magnetite. The crystallites are believed to be a spinel, but further research on the mineralogy of the rock is required before their composition or that of the sulphide is known and the significance of their presence properly understood. The data at present available suggests that the behaviour of the rock may be interpreted generally in terms of Néel's third hypothesis although the details may still be obscure.

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* T.R.M.—thermo-remanent magnetization.

In interpreting reversed Adirondack rocks containing ilmenite–hematite intergrowths Balsey and Buddington (*op. cit.*) considered Néel's third hypothesis was the most likely explanation. They attributed the high coercivity of their reversed rocks and the high ratios of remanent to induced magnetization to the presence of the lower Curie Point component in separated particles of domain size distributed through the component of higher Curie Point. The slight demagnetizing field set up by the latter acts only to direct the spontaneous magnetization of the individual, isolated single domains of the lower Curie Point component. On this explanation the intensity of magnetization is a function of the spontaneous magnetization of the lower Curie Point component and its quantity and is essentially independent of the intensity of the external field.

Although it is clear that mineralogical associations of self-reversing magnetic properties do occur they do not seem to be frequent. According to the suggestion here advanced they are likely in igneous rocks only when the latter have suffered rapid chilling following a period of slow cooling. The temperature at which chilling sets in must be within a very restricted range for an ore of given composition—chilling from too high a temperature would yield a single solid solution phase and chilling from too low a temperature would permit the rhombohedral phase to assume the more stable very weakly ferrimagnetic form. If the intergrowth needs to be on a domain scale chilling from too low a temperature would be adverse to the development of self-reversing properties since it would permit the exsolved bodies to develop on too coarse a scale. But temperature is not the only factor determining the size of the exsolved bodies—composition of the original solid solution is also significant (Edwards 1938, p. 47). The original solid solution should contain comparatively small amounts of the exsolving phase. For a self-reversing intergrowth to result the amount of the exsolving phase must be delicately balanced between that sufficient to cause reversed magnetization in the whole rock and insufficient to exsolve as bodies of too coarse a scale. This balance is especially delicate in igneous rocks where the exsolving phase may have magnetic properties significantly weaker than the host—it may be less so in the ilmenite–hematite intergrowths of metamorphics where exsolved phase and host probably have similar magnetic properties. But the coincidence of appropriate composition and temperature at which rapid cooling sets in is unlikely to be frequent in rocks and this may explain the rarity of examples of self-reversing igneous rocks. In the metamorphics chilling is less probable—here the major factor determining the scale of the intergrowth may be the composition of the original solid solution. The range of composition of solid solutions that could yield self-reversing associations is not yet known.

If the second or fourth of Néel's hyotheses or Graham's hypothesis were applicable to rocks they should acquire a thermo-remanent magnetization parallel to the external field on laboratory cooling from temperatures in excess of the Curie Points of their contained ferrimagnetic minerals (as most reversed rocks do). Parry (1954) quotes Street for an adverse view of Néel's second hypothesis, for which there is, as yet, no evidence of significance in natural occurrences. It requires the formation of a mineral of unknown character. Néel's fourth hypothesis envisages changes that should lead to physical or chemical differences between normal and reversed specimens. Such differences have not been found (Hospers 1953, Clegg, Almond and Stubbs 1954, Bruckshaw 1954). Laboratory heating may be responsible for some alteration and if a component of a self-reversing intergrowth is modified or destroyed by such heating the direction of thermo-remanent magnetization acquired by the rock on cooling may be changed. Conversion of maghemite to hematite would destroy the reversed magnetization if it arose in the way suggested by Graham (1953). Graham's hypothesis depends on the oxidation of magnetite to maghemite; while this is known to occur under certain conditions the more frequent oxidation product of magnetite is hematite. Since maghemite will only develop as an oxidation product of magnetite at temperatures well below 600°c it must acquire its magnetization at temperatures well below its Curie Point and it is questionable how far such magnetization would be stable. Thus while this hypothesis is plausible it is not likely to be applicable in all cases of reversed remanent magnetization and application of it should be dependent on the identification of maghemite in the rock. Exsolution, either continued or initiated through heating, could upset the balance of a self-reversing aggregate and thus modify the magnetic properties of the host rock. But as it is a continuous reaction in the minerals in question it is unlikely to cause sudden changes. The reversed magnetization might be expected to diminish in intensity on the first few thermomagnetic runs but hardly change direction completely with the intensity either remaining constant or increasing. For exsolution on laboratory heating to change the direction of the thermo-remanent magnetization implies the presence before heating of a mechanism for self-reversal. Reasons have just been given why aggregates of self-reversing character are unlikely to have been frequent in rocks and, in any case, are probably restricted to igneous and metamorphic types. Graham (*op. cit.*, p. 255) has suggested that reversed remanent magnetization in sediments may be due in some cases to partial oxidation of contained magnetite to maghemite after deposition through the agency of percolating heated solutions. Indications of such alteration should be apparent on a study of the rocks and although the hypothesis may be applicable in a few cases it is not likely to explain all reversed sediments which acquire a remanent magnetization parallel to the external field on laboratory heating and cooling. Nor can such behaviour be explained by changes taking place on laboratory heating. A belief in periodic reversals of the earth's magnetic field seems to be justified simply by the presence of reversed sedimentary rocks. That reversed remanent magnetizations can be due to other causes is evident from the Haruna and Adirondack rocks but of the mechanisms suggested for self-reversal only Néel's third hypothesis seems likely to explain more than isolated examples. His first and second hypotheses are probably not applicable to natural rocks, his fourth and Graham's hypothesis are unlikely to have wide application. Unless there is some obscure mechanism still undiscovered the frequent occurrence of reversed magnetizations in rocks would seem to imply periodic reversal of the earth's field.

Throughout the preparation of this paper I have profited much from discussions with my colleagues on the staff of the Department of Geology, University of Manchester, though I alone must be responsible for opinions here expressed. To them I tender sincere thanks.

Note added in proof

Since this article was written Professor R. Chevallier has kindly allowed me to see the manuscript of a paper " Titanomagnétites et Ilménites ferromagnétiques " by R. Chevallier, J. Bolfa and Mlle. S. Mathieu which will shortly appear in the *Bulletin de la Societe Française de Mineralogie et de Cristallographie.*

In the interpretation of the magnetic properties of the $Fe_3O_4.FeTiO_3$ series of solid solutions these authors have also postulated a cubic form of $FeTiO_3$ ($\gamma FeTiO_3$) proposing for it the structural formula

$$Fe^{++}_{2/3}\,\square_{1/8}(Ti^{++++}_{4/3}Fe^{++}_{2/3})O_4$$

of spinel type where □ indicates a vacant site in the structure normally occupied in a spinel, the contents of the brackets indicate the cations in 6-fold co-ordination, the cations outside the brackets indicate those in 4-fold co-ordination. For intermediates between Fe_3O_4 and $\gamma FeTiO_3$, which may be expressed as $yFe_3O_4(1-y)Fe_{4/3}Ti_{4/3}O_4$, they suggest

$$Fe^{+++}_{1/3(2+y)}\,\square_{1/3(1-y)}(Fe^{+++}_{1/3(5y-2)}Fe^{++}_{1/3(4-y)}Ti^{++++}_{4/3(1-y)})O_4.$$

Such structures would conform to the rule of Verwey that Fe^{+++} ions preferentially enter the 4-fold co-ordination sites.

Revised values for the intensity of saturation magnetization at 20°c are reported and used to estimate the intensity of saturation magnetization at 0°K ($\sigma_{\infty 0^\circ K}$). Values theoretically deduced for intermediates of the suggested structures correspond quite well with these estimated values but tend to be consistently slightly higher even though the number of Bohr magnetons assigned to the Fe^{++} ions was 4.

The revised values do not support the structures postulated earlier in the present paper for such intermediates. But if the Fe^{++} ions in 4-fold co-ordination are replaced by Fe^{+++} and Ti^{++++} in the approximate ratio 3 : 1 with the Fe^{++} ions of the structure all in the 6-fold co-ordination positions the correspondence between experimental and theoretical data is good. The corresponding structural formula on this interpretation $Fe^{+++}_{1/4(3+y)}Ti^{++++}_{1/4(1-y)}(Fe^{++}_{1/4(7y-3)}Fe^{++}_{1/3(4-y)}Ti^{++++}_{13/12(1-y)}\square_{1/3(1-y)})O_4$, differs from the suggestion of Chevallier and his co-authors in

(1) the position of the vacant sites,

(2) the presence of Ti^{++++} in 4-fold co-ordination positions. Gorter has already shown that in certain other ferrimagnetic spinels containing Ti^{++++} and Fe^{+++} some of the former ions accompany the latter into the 4-fold co-ordination positions (E. W. Gorter 1954, *Philips Res. Rep.*, **9**, 403–443). Recognition that this is possible permits the observed intensities of saturation magnetization to be explained without the necessity of keeping some Fe^{++} ions in 4-fold co-ordination as formerly appeared necessary.

The second of the above structures is preferred since (*a*) it gives a better correspondence between theoretical and revised observed data, (*b*) the theoretical values deduced for the first of the two structures are the lowest possible when the vacant sites are 4-fold co-ordination positions. No ionic rearrangement can reduce them further. Even so they are still high. On the other hand by slightly modifying the proportion of Fe^{+++} and Ti^{++++} in 4-fold co-ordination positions in the second structure complete identity of theoretical and observed data is possible.

If exsolution of solid solutions having the second of the above structures into a spinel of the Fe_3O_4–Fe_2TiO_4 series and a rhombohedral mineral of the $FeTiO_3$–Fe_2O_3 series occurs, the possibilities involving the least ionic migration result in ferrimagnetic rhombohedral lattices being exsolved. The suggestions advanced in the body of this paper are not significantly affected by the slight modification now made to the suggested structure of the Fe_3O_4–$FeTiO_3$ intermediates.

Chevallier and his colleagues also report the results of investigations of synthetic magnetic rhombohedral minerals and the iserines, which they confirm are magnetic ilmenites. They show that magnetic ilmenites range in composition from $FeTiO_3$ to $\frac{1}{3}Fe_2O_3 \cdot \frac{2}{3}FeTiO_3$, the measured intensity of magnetization rising with increasing Fe_2O_3 content. Their studies of the iserines indicate that in this group of minerals the chemical composition does not determine the magnetic properties and they suggest the possible co-existence in a single crystal of para- and ferromagnetic domains in interpretation of their results, particularly the way in which the specimens lose their magnetization on heating. Further structural studies on these minerals, which are clearly needed, are being planned by these French workers.

References

Abrahams, S. C., and Calboun, B. A., 1953, *Acta Cryst.*, **6,** 105.

Akimoto, S., 1951, *J. Geomag. Geoelect.*, **3,** 47 ; 1954, *Ibid.*, **6,** 1.

Baker, G., 1952, *Am. Mineralogist*, **37,** 567.

Balsey, J. R., and Buddington, A. F., 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly A.T.M.E.*, I.U.G.G., 22.

Balsey, J. R., Buddington, A. F., and Fahey, J. J., 1952, *Trans. Am. Geophys. Union*, **33,** 320.

Barth, T. F. W., and Posnjak, E., 1932, *Zeit. f. Kristallographie*, **82,** 325.

Basta, E. Z., 1953, *Ph.D. thesis*, Bristol.

Bénard, J., 1939, *Ann. Chim.*, **12,** 5.

Bénard, J., and Chaudron, G., 1937, *C. R. Acad. Sci., Paris*, **204,** 776.

Benoit, R., 1952, *C. R. Acad. Sci., Paris*, **234,** 2175.

Bertaut, F., 1951, *J. Phys. Radium*, **12,** 252 ; 1952, *C. R. Acad. Sci., Paris*, **234,** 1295.

Bickford, L. B., 1949, *Phys. Rev.*, **76,** 137.

Bragg, W. L., 1937, *The Atomic Structure of Minerals* (New York : Cornell University Press).

Brindley, G. W., 1951, *X-ray Identification of Clay Minerals* (London : Min. Soc. (ed.)).

Bruckshaw, J. McG., 1954, *Science Progress*, **42,** 406.

Bruckshaw, J. McG., and Robertson, E. I., 1949, *Mon. Not. Roy. Ast. Soc., Geophysical Suppl.*, **5,** 8, 308.

Brun, A., 1924, *Arch. Sci. Phys. Nat. Genève*, **6,** 244.

Chaudron, G., and Forestier, H., 1924, *C. R. Acad. Sci., Paris*, **179,** 763.

Chayes, F., 1949, *Am. Mineralogist*, **34,** 1.

Chevallier, R., 1951, *J. Phys. Radium*, **12,** 172.

Chevallier, R., and Girard, J., 1950, *Bull. Soc. Chem. France*, **5, 17,** 576.

Chevallier, R., and Mlle. Mathieu, S., 1937, *C.R. Acad. Sci., Paris*, **204,** 854 ; 1943, *Ann. Physique*, **18,** 258.

Chevallier, R., Mlle. Mathieu, S., and Vincent, E. A., 1954, *Geochimica Cosmochimica Acta*, **6,** 27.

Chevallier, R., and Pierre, J., 1932, *Ann. Physique*, **10, 18,** 383.

Clegg, J. A., Almond, M., and Stubbs, P. H. S., 1954, *Phil. Mag.* (7), **45,** 583.

Creer, K. M., Irving, E., and Runcorn, S. K., 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly, A.T.M.E.*, I.U.G.G., 1.

Curnow, C. E., and Parry, L. G., 1954, *Nature, Lond.*, **174,** 101.

Daly, R. A., 1933, *Igneous Rocks and the Depths of the Earth* (New York).

Edwards, A. B., 1938, *Proc. Australasian Inst. Min. and Met.*, New Series **110,** 39 ; 1947, *Textures of the ore minerals and their significance* (Melbourne : Austr. Inst. Min. and Met. Inc.) ; 1949, *Am. Mineralogist*, **34,** 759.

Ernst, T., 1943, *Zeit. angew. Min.*, **4,** 394.

Foslie, S., 1928, *Fennia*, **50,** 1.

Goldschmidt, V. M., 1911, *Die Kontaktmetamorphose im Kristianiagebiet Vidensk. Skr. I Math.-nat., kl.* 1911, no. 1 ; 1954, *Geochemistry* (Oxford).

Goldschmidt, V. M., Barth, T. F. W., and Lunde, G., 1926, *Geochemische Verteilungsgesetze der Elemente, Norske Vidensk. Akad. Skr.* 7.

Gorter, E. W., and Schulkes, J. A., 1953, *Phys. Rev.*, **90,** 487.

Gottschalk, V. H., 1935, *Physics*, **6,** 27.

Graham, J. W., 1949, *J. Geophys. Res.*, **54,** 131 ; 1953, *Ibid.*, **58,** 243.

Greig, J. W., Posnjak, E., Merwin, H. E., and Sosman, R. B., 1935, *Am. J. Sci.*, **30,** 239.

Grieve, J., and White, J., 1939, *J. Roy. Tech. Coll. Glasgow*, **4,** 441.

Griffiths, D. H., 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly A.T.M.E.*, I.U.G.G., 63.

Guillaud, C., 1951a, *J. Phys. Radium*, **12,** 239 ; 1951b, *Ibid.*, **12,** 489.

Hägg, G., 1935, *Zeit. Physik. Chem.* B, **29,** 95.

Hägg, G., and Sucksdorf, I., 1933, *Zeit. Physik. Chem.* B, **22,** 444.

Hallimond, A. F., 1953, *Manual of the Polarizing Microscope* (York : Cooke, Troughton and Simms Ltd.), 2nd Edition.

Hámos, L. V., and Stscherbina, W., 1933, *Nachr. Ges. Wiss. Göttingen*, math.-phys. kl. No. 34.

Haraldsen, H., 1937, *Zeit. f. anorg. allg. Chem.*, **231,** 78.

Harker, A., 1939, *Metamorphism* (London).

Haul, P., and Schoon, T., 1939, *Zeit. Physik. Chem.* B, **44,** 216.

Hawkins, H. H., 1932, *Am. Mineralogist*, **17,** 157.

Henry, N. F. M., Lipson, H., and Wooster, W. A., 1951, *The Interpretation of X-ray Diffraction Photographs* (London).

Hess, H. H., 1941, *Am. Mineralogist*, **26,** 515 and 573.

Hospers, J., 1953, *Proc. Kon. Ned. Akad. Wet.* B, **56,** 467 ; 1954, *Ibid.*, **57,** 112.

Johnson, E. A., Murphy, T., and Torreson, O. W., 1948, *Terr. Mag.*, **53,** 349.

Jouravsky, G., Charczenko, P., and Choubert, G., 1933, *C.R. Acad. Sci., Paris*, **197,** 522.

Kawai, N., Kume, S., and Sasajima, S., 1954, *Proc. Japan. Acad.*, **30,** 588.

Kato, K., Takagi, A., and Kato, I., 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly A.T.M.E.*, I.U.G.G., **60.**

Kennedy, G. C., 1948, *Am. J. Sci.*, **246,** 529.

Koenigsberger, J. G., 1938, *Terr. Mag.*, **43,** 119 and 299.

Mason, B., 1943, *Geol. Fören. Förhandl.*, **65,** 95.

Mercanton, P. L., 1926, *C.R. Acad. Sci., Paris*, **182,** 859 ; 1931, *Ibid.*, **192,** 978 ; 1932, *Ibid.*, **194,** 1371.

Michel, A., 1937, *Ann. Chim.*, **3,** 317.

Michel, A., and Chaudron, G., 1935, *C.R. Acad. Sci., Paris*, **201,** 1191.

Michel, A., Chaudron, G., and Bénard, J., 1951, *J. Phys. Radium*, **12,** 189.

Michel, A., and Pouillard, E., 1948, *Bull. Soc. Chim. France*, **962.**

Mogensen, E., 1946, *Geol. Fören. Förhandl.*, **68,** 578.

Nagata, T., 1951, *Nature, Lond.*, **169,** 704 ; 1953 a, *Rock Magnetism* (Tokyo) ; 1953 b, *Nature Lond.*, **172,** 630 and 850.

Nagata, T., and Akimoto, S., 1950, *J. Geomag. Geoelect.*, **2,** 29.

Nagata, T., Akimoto, S., and Uyeda, S., 1953, *J. Geomag. Geoelect.*, **5,** 168 ; 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly A.T.M.E.*, I.U.G.G., 29.

Nagata, T., Uyeda, S., and Akimoto, S., 1952, *J. Geomag. Geoelect.*, **4,** 22.

Nagata, T., Uyeda, S., Akimoto, S., and Kawai, N., 1952, *J. Geomag. Geoelect.*, **4,** 102.

Nagata, T., Rikitake, T., and Akasi, K., 1943, *Bull. Earthquake Research Inst. Tokyo*, **21,** 276.

Nagata, T., and Watanabe, T., 1950, *G.N., Tokyo University*, **3,** No. 21.

Néel, L., 1949, *Ann. Physique*, **4,** 249 ; 1951, *Ann. Geophys.*, **7,** 90 ; 1953, *Rev. Mod. Physics*, **25,** 58.

Nelson, J. B., and Riley, D. P., 1945, *Proc. Phys. Soc.*, **57,** 160.

Newhouse, W. H., 1936, *Bull. Geol. Soc. America*, **47,** 1.

Nieland, H., 1931, *Chemie der Erde*, **6,** 591.

Ödman, O. H., 1932, *Geol. Fören. Förhandl.*, **54,** 285.

Osborne, F. F., 1928, *Econ. Geol.*, **23,** 442.

Palanche, C., Berman, H., and Frondel, C., 1944, *Dana's System of Mineralogy*, 7th Edition (New York).

Parry, J. H., 1954, *Tech. Comm. of Palaeomagnetism, Xth Assembly A.T.M.E.*, I.U.G.G., **44.**

Phillips, R., 1954, Personal comm. to Dr. S. K. Runcorn.

Phillips, R., and Vincent, E. A., 1954, *Geochimica Cosmochimica Acta*, **6,** 1.

Posnjak, E., and Barth, T. F. W., 1934, *Zeit. f. Kristallographie*, **88,** 271.

POUILLARD, E., 1950, *Ann. Chimie*, **5,** 164.

POUILLARD, E., and MICHEL, A., 1949, *C.R. Acad. Sci., Paris*, **228,** 1232.

RAMDOHR, P., 1926, *Neues Jahrb. Min. Geol., Beil. Band* **54,** 320 ; 1950, *Die Erzmineralien und ihre Verwachsungen*, (Berlin : Akad. Verlag) ; 1953, *Econ. Geol.*, **48,** 677.

ROBERTS, H. S., 1935. *J. Am. Chem. Soc.*, **57,** 1034.

ROCHE, A., 1950, *C.R. Acad. Sci., Paris*, **230,** 113 ; 1951, *Ibid.*, **233,** 1132.

ROOKSBY, H. P., and WILLIS, B. T. M., 1953, *Acta. Cryst.*, **6,** 565.

ROQUET, Mlle. J., 1947, *C.R. Acad. Sci., Paris*, **224,** 1418.

ROTH, W. A., and BERTRAM, W., 1929, *Zeit. Elektroch.*, **35,** 306.

SCHNEIDERHÖHN, H., and RAMDOHR, P., 1934, *Lehrbuch der Erzmikroskopie*, Band I (Berlin).

SCHNEIDERHÖHN, H., 1952, *Erzmikroskopisches Praktikum* (Stuttgart).

SCHWELLNUS, C. M., and WILLEMSE, J., 1943, *Trans. Geol. Soc. S. Africa*, **46,** 23.

SHORT, M. M., 1948, *Microscopic Determination of the Ore Minerals*, *Bull.* **914,** U.S. Geol. Surv., 2nd. edition—corrected and expanded 1948 printing.

SHULL, C. G., WOLLAN, E. O., and KOEHLER, W. C., 1951, *Phys. Rev.*, **84,** 912.

SOSMAN, R. B., and POSNJAK, E., 1925, *J. Acad. Sci. Washington*, **15,** 329.

STSCHERBINA, W. (Sčerbina), 1939, *C.R. Acad. Sci., U.S.S.R.*, **22,** 503.

TOMBS, N. C., and ROOKSBY, H. P., 1951, *Acta Cryst.*, **4,** 474.

TORRESON, O. W., MURPHY, T., and GRAHAM, J. W., 1949, *J. Geophys. Res.*, **54,** 111.

TURNER, F. J., 1948, Mineralogical and Structural Evolution of the Metamorphic Rocks, *Memoir* 30, *Geol. Soc. America.*

VASSAR, H. E., 1925, *Am. Mineralogist*, **10,** 123.

VERWEY, E. J. W., 1935, *J. Chem. Phys.*, **3,** 592.

WAGER, L. R., and DEER, W. A., 1939, *Medd. om Grønland*, Band 105, Nr. 4.

WAGNER, P. A., 1928, *Mem. Geol. Surv. S. Africa*, **26,** 29.

WILLIS, B. T. M., and ROOKSBY, H. P., 1952, *Proc. Phys. Soc.* B, **65,** 950.

Some Theoretical Aspects of Rock-Magnetism

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Summary

The memoir is devoted to a brief theoretical study of the most typical magnetic properties of rocks. In particular §§ 3–16 are on ferrimagnetism, §§ 17–35 on single domain particles and §§ 36–57 on large multi-domain particles.

Theoretical studies are made of the following aspects of the subject and compared with the experimental results : remanent magnetization (§ 38), initial susceptibility (§ 39), variation with applied field of thermo-remanent magnetization (abbreviated to T.R.M.) (§§ 40, 41, 57), the ratio Q_k of T.R.M. acquired in a given field to the induced magnetization in the same field (§ 42), the additivity of partial T.R.M.’s in the case both of small grains (§ 28) and large grains (§ 57).

Considerable space is devoted to the magnetic ‘ viscosity ’ due to thermal agitation in small grains (§§ 24–27) and in larger ones (§§ 49–56). Expressions are given for magnetic ‘ viscosity ’ in the range of Rayleigh’s relations (§ 51) particularly with a demagnetizing field present (§ 54). The theoretical and experimental results on the irreversible decrease in isothermal remanent magnetization are briefly quoted both for small (§ 30) and large (§ 55) grains.

Different reversing mechanisms are reviewed which could cause a negative T.R.M., that is one directed in the opposite sense to the field applied during cooling. Some are related to negative Weiss–Heisenberg exchange forces : reversal by diffusion involving ionic exchange between the two sub-lattices in a ferrimagnetic (§ 7), reversal by anomalous thermal variation is spontaneous magnetization (§§ 11, 12), reversal by diffusion with complete change of composition (§ 16). The others are effects of the demagnetizing field : reversal in mixtures of two constituents with different Curie Points (§§ 31–34), reversal by segregation, allotropy and chemical alteration (§ 35). The actual examples so far known are recalled.

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§ 1. Introduction

In the general scheme of magnetic theory, the problems of the magnetic properties of rocks are distinguished by certain peculiarities which it is convenient to make clear at the outset.

In the first place, the carriers of magnetic properties are the various more or less pure oxides of iron, magnetite, titanomagnetites, hematite, maghemite, etc. . . . , that is, substances which are ferrimagnetic or antiferromagnetic rather than classical ferromagnetics. A notable result is that the thermal variation of saturation magnetization of rocks can be of very different types from that of iron or nickel.

A second point to be emphasized is that the magnetic constituents are a small proportion, perhaps a few per cent, distributed amongst the practically non-magnetic bulk of the rock. The problem is that of magnetic grains more or less far from one another so that the demagnetizing field due to shape is very important.

A third point is that, since the geophysicist is especially interested in the magnetic properties of rocks relative to the earth's field, the properties in fields small compared with the coercive force are of particular interest.

Finally, magnetic viscosity and the effects of time on magnetic phenomena in general are of great importance, because the time scale concerned is the geological one.

§ 2. THE THREE PROCESSES OF CHANGE IN MAGNETIZATION

A detailed study and investigation of the magnetic properties of rocks could be the basis of a complete treatise on magnetism, and naturally there is no place for that here. We shall consider only the most important particular points, referring for the rest to the classical works on ferromagnetism(1).

According to Weiss' already classic theory, a ferromagnetic substance is divided into *elementary domains* of varying size within which the magnetization is uniform. The direction of this magnetization varies from one domain to another but its magnitude J_s remains constant and is called the *spontaneous magnetization*. In practice, J_s depends only on the temperature T and the temperature at which it falls to zero is called the Curie Point. On the other hand the shape and size of the elementary domains as well as the orientation of their spontaneous magnetizations depend on many factors : the applied field, the internal demagnetizing field and that due to shape, magneto-crystalline and magneto-elastic couplings, the presence of dislocations or impurities, etc.

The magnetization of ferromagnetic bodies, considered as a function of magnetic field and of temperature, thus depends on three distinct processes : (*a*) the reversible change in the *magnitude* of the spontaneous magnetization with temperature ; (*b*) the changes of direction or rotations of the spontaneous magnetization within the domains, whose boundaries remain fixed ; (*c*) the displacement of the walls separating elementary domains whose direction of magnetization remains fixed.

We have to study the effects of these different processes on the properties of rocks and baked clays.

THE FERRIMAGNETISM OF ROCKS

§ 3. DEFINITION OF FERRIMAGNETISM

The simplest kind of ferromagnetic substance is typified by iron: all the atoms are identical and have the same permanent magnetic moment. A coupling exists between the moments of neighbouring atoms which favours the parallel orientation of these moments so that, at temperatures low enough for the energy of thermal agitation kT to be small compared with the energy of coupling, all the atomic moments are parallel to each other: this is the strict definition of *ferromagnetism*.

But more complicated kinds can be imagined, such as where there are two types of atoms with couplings of such magnitude and sign that at low temperatures the atomic moments of one type all point in one direction and those of the other type all in exactly the opposite direction. One is then dealing with ferrimagnetism⁽²⁾.

In both cases a small element of volume dv of the substance, large compared with atomic dimensions, has a permanent spontaneous magnetic moment $J_s\,dv$, where J_s is the spontaneous magnetization defined above.

§ 4. THE SIMPLE INVERSE FERRITES

Many of the ferromagnetic constituents of rocks, in particular the titanomagnetites, are of the spinel type with properties more or less analogous to those of the ferrites MFe_2O_4, where M is a divalent metal. In these ferrites the metallic ions can occupy two crystallographically different types of sites: the lattice has, per unit molecule, one tetrahedral site A, surrounded by 4 oxygen atoms and two octahedral sites B surrounded by 6 oxygen atoms.

It has been shown experimentally⁽³⁾ that several types of spinel ferrites exist: the *normal ferrites* have the M ion on the A site and the two Fe^{+++} ions on the B sites, as in zinc ferrite. These ferrites are not magnetic. There are also the *inverse ferrites* in which the A site is occupied by an Fe^{+++} ion and one of the B sites is occupied by the M ion and the other by the second Fe^{+++} ion; these ferrites are magnetic.

The interatomic couplings are, from a magnetic point of view, most powerful when they act between an ion on an A site and one on a B site; these AB interactions are *negative* and tend to align the atomic moments of the two interacting atoms antiparallel. The interactions between atoms occupying the same types of site, the AA or BB interactions, are generally much weaker and play only a secondary role. Owing to the strong negative AB interactions the magnetic lattice is, at low temperatures, divided into two sub-lattices A and B, corresponding to the A sites and B sites, whose spontaneous magnetizations J_A and J_B are oriented in opposite directions: this is a typical case of *ferrimagnetism*⁽²⁾.

These conclusions were reached from a profound study of the magnetic properties of these substances and have been very directly confirmed by neutron diffraction. Shull and his co-workers have shown(4), for example in magnetite (where M=Fe^{++}), that the magnetic moments of atoms on A sites are in fact antiparallel to those of atoms on B sites. Thus in the inverse ferrites the molecular moment, close to absolute zero, is simply given by the atomic moment of the M ion, since the moments of the Fe^{+++} ions on A sites exactly cancel those of the Fe^{+++} ions on B sites. In fact it is found that with M=Ni^{++}, Co^{++}, Fe^{++}, Mn^{++} the molecular moments of the corresponding ferrites are close to 2, 3, 4 and 5μ_B which are the values of the spin magnetic moments of these ions. The slight remaining differences are probably due to residual orbital moments.

§ 5. THE DISTRIBUTION OF IONS ON THE DIFFERENT SITES IN SPINELS

Assuming that in the ferrites the elementary atomic moments of sub-lattice A are aligned antiparallel to those of sub-lattice B, then the magnetic properties will be closely related to the distribution of cations between the two types of sites. This distribution depends on factors which are not yet fully understood. According to Verwey and Heilmann(3) and Romeijn(5), Zn^{++}, Cd^{++}, Ga^{+++}, In^{+++} and Ge^{++++} ions have a preference for A sites, Ni^{++}, Cr^{+++}, Ti^{++++} and Sn^{++++} ions for B sites while Mg^{++}, Al^{+++}, Fe^{++}, Co^{++}, Mn^{++}, Fe^{+++} and Cu^{++} ions can occupy either A or B sites according to circumstances.

In certain cases, the tendency of the ions to be placed in a definite ordered distribution is feeble enough for the distribution to change considerably with temperature. This effect is observable in $ZnFe_2O_4$ and $NiFe_2O_4$ and is important in $CdFe_2O_4$ while in $MgFe_2O_4$ and $CuFe_2O_4$ a detailed quantitative study has been made of it(6).

Letting w be the energy necessary to transfer a bivalent ion M from a B site to an A site, this transfer being of course accompanied by that of a ferric ion in the opposite direction, and letting y and $1-y$ be the proportions of M ions, on the A and B sites at temperature T, then Boltzmann's law shows that(2)

$$\frac{y(1+y)}{(1-y)^2}=\exp\left(-\frac{w}{kT}\right).$$

Thus y is a function of T. The state of thermodynamic equilibrium at any temperature T can in principle be preserved in false equilibrium at room temperature by quenching. If the atomic moments of Fe^{+++} and M^{++} ions are respectively 5 and m Bohr magnetons, the saturation molecular moment M_s observed at low temperatures will be

$$M_s=[m+2y(5-m)]\mu_B.$$

These ideas have been confirmed by Pauthenet's work(6) on Mg and Cu ferrites in which he followed the variation of saturation moment with the temperature of quenching and found values of w/k equivalent to 1220°K and 1540°K respectively.

If the quenching temperature T is below 500–600°K thermodynamic equilibrium is no longer established at that temperature even after several hours. This shows the possibility of preserving a false equilibrium at room temperature for a time which is long compared with the length of experiments. But this would no longer be true after some tens of millions of years; then the moment M_s of the ferrite considered would correspond to y_0, the value of the equilibrium parameter appropriate for the prevailing temperature T_0. If this true equilibrium state happens to be destroyed, for instance by heating, no laboratory method can ever restore it. This is an example of the important effect that the enormous scale of geological time can have on the physical state of rocks as well as on their magnetic properties.

§ 6. SUBSTITUTED FERRITES: THE CASE OF ALUMINIUM

Important results are given by a study of substituted ferrites such as $NiFe_{2-m}Al_mO_4$, which can be described as $NiFe_2O_4$ in which some Al^{+++} ions have replaced Fe^{+++} ions. If all the Al ions replaced ferric ions on octahedral B sites, a decrease of saturation molecular moment at absolute zero would be observed proportional to the amount m of substituted Al ions. In particular for $m=0{\cdot}4$, the saturation moment ought to be zero and the negative values given by the formula for $m>0{\cdot}4$ would simply correspond to the spontaneous magnetization of sub-lattice A becoming greater than that of sub-lattice B.

In fact as E. W. Gorter has shown(7) this is roughly what happens for well-annealed specimens except that the moment is zero for $m=0{\cdot}62$ showing that a small fraction of the Al^{+++} ions occupy A sites. On the contrary for quenched specimens the moment does not fall to zero and thus never becomes negative even for the composition $NiFeAlO_4$: the necessary conclusion is that in the quenched state a much larger proportion of Al^{+++} ions occupy A sites. Thus annealing causes some Al ions to move from A sites to B sites, giving a decrease of spontaneous magnetization since the number of Fe^{+++} ions, carrying $5\,\mu_B$, on A sites increases. This effect is most marked for $m=1$ when the molecular moment of the quenched specimen is $+0{\cdot}42\,\mu_B$ while that of the annealed one is $-0{\cdot}64\,\mu_B$.

§ 7. CHANGE OF SIGN OF SPONTANEOUS MAGNETIZATION BY ANNEALING

Since the spontaneous magnetization of $NiFeAlO_4$ changes sign on annealing the remanent magnetic moment of a specimen of this substance, magnetized at high temperature and then quenched, must change sign spontaneously on reheating: there is an *inversion of spontaneous magnetization*. This inversion is produced by diffusion of Al ions from A to B. To produce the inversion in the laboratory several hours at 400°C are needed, but the same effect would probably occur at ordinary temperatures in some millions of years. Naturally thi inversion of the spontaneous magnetization involves reversal of any remanent magnetization. From Gorter's data[7] the same inversion effect should occur over the whole range $0{\cdot}62<m<1$. Also it seems probable that the compounds in the range $0{\cdot}50<m<0{\cdot}62$ which in the laboratory always have a positive moment, whether they are quenched or annealed, could, after some millions of years at ordinary temperatures acquire a negative moment: it is only necessary that, at the rather high temperature at which annealing in the laboratory still has a noticeable effect, the equilibrium concentration of the Al^{+++} ions be but slightly positive. Then the lower annealing temperature, made possible by the enormous length of the process, will displace the equilibrium towards negative moments. Such a substance would in all possible laboratory experiments always have a positive thermoremanence but in the course of geological time would acquire a negative spontaneous magnetization and a remanent magnetization opposite to its original one.

This curious behaviour of the ferrites of the type $NiFe_{2-m}Al_mO_4$ is important although similar effects could probably not be observed in the natural substituted magnetites which form many of the ferromagnetic constituents of rocks. The reason is that in the nickel ferrites the magnetic moments of the two sub-lattices A and B are very close $5\,\mu_B$ and $7\,\mu_B$ so that it is much easier for the A sub-lattice to have a greater moment than the B than in magnetite where the moments of the two sub-lattices, at 5 and $9\,\mu_B$ are much less close.

§ 8. SUBSTITUTED FERRITES: THE CASE OF TITANIUM

Many of the ferromagnetic constituents of rocks are titanomagnetites, derived from magnetite Fe_3O_4 by substitution of Ti^{++++} ions for Fe^{+++} ions, together with a change of ionization of an Fe^{+++} ion to an Fe^{++} ion. This gives solid solutions of spinel type with the general formula $Ti_mFe_{3-m}O_4$ which were first studied by Michel and Pouillard[8]. If it is assumed that the Ti^{++++} ions always occupy B sites and that the remaining B sites are filled by Fe^{++} ions, the saturation molecular moment ought to be given by $(4-6m)\mu_B$ in the interval $0<m<0{\cdot}5$ and by $(2-2m)\mu_B$ when $0{\cdot}5<m<1$. The experimental facts are not enough to decide if these suggestions, especially on the distribution of Fe^{++} ions, are correct. All that is known is that the saturation moment and the Curie Point fall regularly as m increases.

Recently Kawai, Kuma and Sasajima[9] have observed that solid solutions of this type, which immediately after quenching have a single clearly defined Curie Point, change gradually so that after several months at room temperature they have two Curie Points, one at about 100°C and the other close to that of magnetite. It is tempting to interpret this change as a segregation into two phases, one rather weakly magnetic and the other near to magnetite.

Finally mention must be made of maghemite which is similar to the cubic sesquioxyde $Fe_2O_3\gamma$ and has a spinel structure rather like that of magnetite but with some B sites empty : it is also a ferrimagnetic.

§ 9. THE THERMAL VARIATION OF THE MAGNETIZATION OF FERRITES

The thermal change of spontaneous magnetization J_s in rocks is particularly interesting as they have generally acquired their natural magnetization in a temperature range close to their Curie Point where J_s is much smaller than at ordinary temperatures. In an assemblage of elementary domains, in which the boundaries and direction of spontaneous magnetization of each domain remain fixed, the mean magnetization of the aggregate will be proportional to, and vary reversible with, J_s. Thus a small magnetization acquired near the Curie Point can increase reversibly during cooling of the specimen. As will be shown later (cf. §§ 32–35) this can have curious results in mixtures of several ferromagnetic constituents with different Curie Points. For most ordinary ferromagnetic substances such as iron, nickel, cobalt and their alloys, the curves of J_s against temperature have very similar shapes, typically a slow variation of J_s at low temperatures (less than 10% up to $T=0{\cdot}6\theta$) and a rapid one near the Curie Point θ. In the case of rocks, although the J_s–T curve of pure magnetite is very similar to that of metals, very different types are also found, such as a practically linear change of J_s with T from absolute zero right up to the Curie Point. This variability is typical of the ferrimagnetics.

§ 10. THE MOLECULAR FIELD THEORY APPLIED TO FERRIMAGNETISM

As a first approximation to a theory of the thermal variation of spontaneous magnetization the Weiss molecular field theory can be used. This, being purely phenomenological, replaces the interactions between the elementary magnetic moments by an imaginary magnetic field called the molecular field which is proportional to the magnetization $\mathbf{J}$ and is given by

$$\mathbf{H}_m=N\mathbf{J}$$

where N is the molecular field coefficient.

The magnetization law for a paramagnetic in which the atomic moments are quite independent of each other and can be freely oriented is of the form

$$J=B(H/T).$$

If then a ferromagnetic can be considered as a paramagnetic which is magnetized and given its spontaneous magnetization J_s by its own molecular field H_m, J_s will be the solution of the implicit equation

$$J_s=B(NJ_s/T).$$

The classical discussion of this equation need not be given here except to recall that the shape of the $J_s(T)$ curve depends on the form of the function $B(H/T)$ which itself depends on the value of j, the total angular momentum quantum number of the magnetic atom concerned. The $J_s(T)$ curves of ferromagnetic metals correspond roughly to the value $j=\frac{1}{2}$, indicating that the magnetic carriers are isolated spins.

Néel(10) has slightly modified the molecular field theory by supposing H_m to be proportional to the mean magnetic moment of closely neighbouring atoms. For substances like the ferrimagnetics having two sub-lattices A and B with magnetizations $\mathbf{J}_a$ and $\mathbf{J}_b$ two molecular fields must be considered, $\mathbf{H}_a$ acting on atoms on A sites and $\mathbf{H}_b$ on those on B sites. They are given by

$$\mathbf{H}_a=n_{aa}\mathbf{J}_a+n_{ab}\mathbf{J}_b,$$
$$\mathbf{H}_b=n_{ab}\mathbf{J}_a+n_{bb}\mathbf{J}_b,$$

involving three molecular field coefficients n_{aa}, n_{ab}, n_{bb} representing the AA, AB and BB interactions. If $B_a(H/T)$ and $B_b(H/T)$ are the paramagnetic magnetizations of ions on the A and B sub-lattices respectively, it can be shown that, in the absence of an applied field, the system has a spontaneous magnetization $\mathbf{J}_s$

$$\mathbf{J}_s=\mathbf{J}_a+\mathbf{J}_b.$$

It is the vector sum of the two partial spontaneous magnetizations of the two sub-lattices A and B, J_a and J_b which are solutions of the complementary equations

$$\mathbf{J}_a=B_a(\mathbf{H}_a/T),$$
$$\mathbf{J}_b=B_b(\mathbf{H}_b/T).$$

In the important case of the ferrites, n_{ab} *is negative and large compared with the other two coefficients* n_{aa} *and* n_{bb}. The partial spontaneous magnetizations are then antiparallel and J_s is simply the arithmetic difference between J_a and J_b. If these have different absolute values the system will have a finite resultant spontaneous magnetization, that is to say an apparent ferromagnetism, created by negative interactions.

The two partial spontaneous magnetizations J_a and J_b disappear together at the Curie Point θ above which simple paramagnetism is observed. However the reciprocal of the susceptibility χ does not vary linearly with temperature, following the Curie–Weiss law of ordinary ferromagnetics, but according to a hyperbolic law of the form

$$\frac{1}{\chi}=\frac{T}{C}+\frac{1}{\chi_0}-\frac{\sigma}{T-\theta},$$

where C is the theoretical Curie constant of the ions present and χ_0, σ and θ depend on n_{aa}, n_{bb} and n_{ab}. This hyperbolic variation is characteristic of ferrimagnetic substances.

The three coefficients of the molecular field can be found from a study of the susceptibility above the Curie Point(11) and hence the thermal variation of spontaneous magnetization below the Curie Point can be deduced without recourse to any other data. Good agreement between theory and experiment has been found by Pauthenet(6) for nickel, cobalt and iron ferrites and more recently by Clark and Sucksmith⁽¹²⁾ for manganese ferrite.

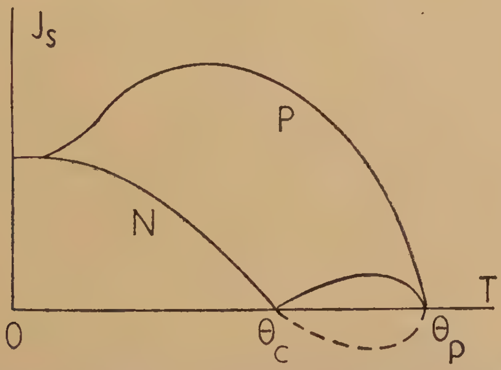
Despite these good agreements it must not be forgotten that theory based on the molecular field approximation sometimes gives very inaccurate results as in the case of linear chains of atoms.

§ 11. INVERSION OF THE SPONTANEOUS MAGNETIZATION

Although the ferrites mentioned above already have a very different thermal change of spontaneous magnetization from the classical ferromagnetics, much more extraordinary curves can be conceived. That this is likely can be seen *a priori*, given the number of different factors on which the variation of $J_s(T)$ depends: values of j for the A and B ions, of the ratios n_{aa}/n_{ab} and n_{bb}/n_{ab}, and of the spontaneous magnetizations at absolute zero J_{as} and J_{bs} of the sub-lattices A and B. Curious forms are found especially when J_{as} and J_{bs} have closely similar *magnitudes* as in observing their slight difference their own irregularities are magnified.

Thus curves of type P (fig. 1) are possible, showing an *increase* of spontaneous magnetization from absolute zero to a maximum value. Such curves have actually been observed by E. W. Gorter⁽⁷⁾ in ferrites of general formula $Ni_{1\cdot5-a}Mn_aFeTi_{0\cdot5}O_4$ when a lies in the range 0·4–0·675.

Fig. 1

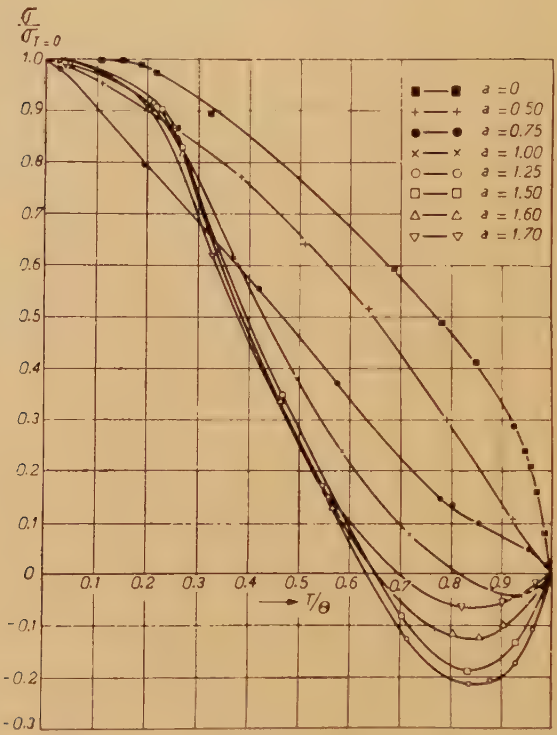


Two unusual types of thermal change of spontaneous magnetization characteristic of ferrimagnetic substances.

N is an even more remarkable type of curve in which the spontaneous magnetization decreases normally and disappears for the first time at temperature θ_c but then begins to increase again, reaches a maximum and finally disappears at a Curie Point θ_p. θ_c is not a Curie Point but only the temperature at which the spontaneous magnetization changes sign. Below θ_c the spontaneous magnetization J_a of sub-lattice A, say, is greater than that of B while above θ_c the reverse is true. θ_c can be called the *compensation temperature* at which the absolute values of the spontaneous magnetizations of the two sub-lattices are equal. Two conditions would appear to favour the appearance of this curious phenomenon : the two sub-lattices must have rather similar saturation magnetizations and at the same time rather different values of j.

This type of curve whose existence was forecast theoretically in 1948 was found some years later by E. W. Gorter(7) in the mixed ferrites $Li_{0 \cdot 5}Fe_{2 \cdot 5-a}Cr_aO_4$ for values of a between 1·00 and 1·70 (cf. fig. 2).

Fig. 2



Curves of thermal change of spontaneous magnetization in the ternary ferrites $Li_{0 \cdot 5}Fe_{2 \cdot 5-a}Cr_aO_4$ after E. W. Gorter.

The interpretation of θ_c as a temperature at which the spontaneous magnetization changes sign can be confirmed by an elegant experiment. A remanent magnetization is given to the specimen at a temperature below θ_c. It is then heated in a zero magnetic field past θ_c and the remanent magnetization is found to change sign spontaneously when the temperature of the specimen is θ_c. This is a very neat and direct proof of the existence of two magnetic sub-lattices in ferrites.

More recently other instances of the N type have been found in a new group of ferrites discovered by Forestier. These are the rare earth ferrites of general formula $Fe_2M_2O_6$ when M is a trivalent rare earth element(13). Guiot-Guillain, Pauthenet and Forestier(14) have shown if M is Gd, Er or Dy these ferrites have N-type curves. They have also shown that the first point where the spontaneous magnetization disappears is in fact a compensation temperature by means of the spontaneous reversal of remanent magnetization at θ_c. Néel(15) has shown that as there are probably three sub-lattices the explanation is still more complicated. In other respects the magnetic properties of these rare earth ferrites are somewhat similar to those of rhombohedral ferric oxide $Fe_2O_3\alpha$ which will be considered later.

§ 12. DISTINCTION BETWEEN COMPENSATION TEMPERATURE AND CURIE POINT

Although the spontaneous magnetization disappears at the compensation temperature just as at the Curie Point, the possibility of thermo-remanent magnetization in a small field H which distinguishes the Curie Point, does not occur at the compensation temperature. In fact at this temperature while the couple HJ_s exerted by the external field on the resultant spontaneous magnetization J_s falls to zero because J_s falls to zero, the perturbing magnetocrystalline and magnetoclastic forces remain finite as they are of the order of the squares $J_a{}^2$, $J_b{}^2$ of the partial spontaneous magnetizations : thus there is no possibility of magnetization by a small field.

The result is that if a substance with a compensation point θ_c is acted on by a small field H when cooled from above its Curie Point, it will acquire near the latter a thermo-remanent magnetization (or T.R.M.) which from a few tens of degrees lower, will change practically reversibly remaining proportional to the spontaneous magnetization, independent of any variations in the applied field provided this remains of the order of H. In particular the T.R.M. will change sign with the spontaneous magnetization at θ_c. At room temperature such a substance will then have a T.R.M. opposite to the sense of the field to which it is due.

It should be noticed that this reversed T.R.M. is fundamentally due to a difference between the thermal changes of the two sub-lattices. It is a different mechanism from that described before (§ 7) involving an exchange of ions between the two sub-lattices below the Curie Point.

§ 13. TRIANGULAR SYSTEMS

Finally mention should be made in the study of ferrimagnetism of more complicated phenomena which appear if within say the B sub-lattice, negative BB interactions occur which are comparable with the AB interaction between the sub-lattices, the B sub-lattice can then be divided in its turn into two secondary sub-lattices. Such are the *triangular* systems studied by Yafet and Kittel(16) ; no certain examples of them are yet known.

§ 14. RHOMBOHEDRAL FERRIC OXIDE

Rhombohedral ferric oxide $Fe_2O_3\alpha$, the mineral *hematite*, is an important ferromagnetic constituent of rocks and baked clays. Unfortunately its magnetic properties are not yet fully understood despite much study. The effects(17) are approximately those of a paramagnetism only slightly dependent on temperature, with a specific susceptibility of about 20×10^{-6}, superimposed on a very feeble ferromagnetism with a molecular saturation magnetization of about one-hundredth of a Bohr magneton and a Curie Point at 675°C, definitely higher than that of magnetite (595°C).

The paramagnetism derives from a *fundamental antiferromagnetism* due to the distribution of ferric ions on two equal sub-lattices with equal and opposite spontaneous magnetizations. This distribution was suggested by detailed analysis of the magnetic properties and has subsequently been directly confirmed by neutron diffraction (Shull *et al.*(4)). At temperatures below 250°K, the direction of antiferromagnetism, that is the direction to which the spontaneous magnetizations of the two sub-lattices are parallel or antiparallel, lies in the basal plane of the crystal(18) and can turn freely in that plane. The result is that the paramagnetic susceptibility, which is related to distortion of the antiparallel arrangement of spontaneous magnetizations under the action of the applied field, is practically independent of the crystallographic orientation of this field. On the other hand, above 250°K, the direction of antiferromagnetism changes and becomes parallel to the ternary axis of the crystal with the result that the susceptibility becomes much smaller in this direction than in the basal plane, as is found experimentally.

The temperature at which ordering in the two antiferromagnetic sub-lattices disappears (the Néel temperature) is probably 675°C because there is, at this temperature, a large specific heat anomaly which, having a magnitude comparable to that of magnetite, cannot be attributed to the feeble ferromagnetism.

The problem of the superimposed ferromagnetism is much more difficult. It has sometimes been thought, owing to the low value of the saturation magnetization, that it was due to ferromagnetic impurities such as magnetite or the cubic sesquioxide $Fe_2O_3\gamma$, but this hypothesis runs into difficulties over the change of magnetic properties according to thermal treatment. Also it has been shown that the ferromagnetism is oriented with respect to the lattice; for instance, above 250°K, the ferromagnetic part of the magnetization is much greater in directions in the basal plane than along the ternary axis. To explain this it has been suggested that the ferromagnetism is due to small crystals of magnetite, deformed and oriented by intergrowth in the larger crystals of the sesquioxide. This explanation may be partly true in some cases, but it seems more likely that the source is rather in lattice defects, such as errors in the regular alternation of layers of iron atoms magnetized antiparallel, which defects might be related to dislocations of the lattice;

there would then be a sort of ferromagnetic plane surrounded by an antiferromagnetic matrix. Or it could be described as an imperfection in the antiferromagnetism of the rhombohedral sesquioxide which caused a slight asymmetry between the two sub-lattices and thus produced a small resultant spontaneous magnetization: in general there would be a slight ferrimagnetism. The strongest argument for this hypothesis is the coincidence of the ferromagnetic Curie Point with the Néel temperature of the fundamental antiferromagnetism.

Whether they be due to impurities or to lattice defects, it seems that the magnetic properties of $Fe_2O_3\alpha$ can be represented as those of very small ferromagnetic domains, having the properties of hysteresis, buried in a paramagnetic matrix. The magnetization of the matrix is always small and proportional to the applied field so that it is of little interest in rock-magnetism.

§ 15. THE ILMENITE–HEMATITE SERIES

Another series of compounds occurs in rocks, with the general formula $Fe_{2-m}Ti_mO_3$ which can be considered(19) as a combination in varying proportions of ilmenite $FeTiO_3$ and hematite Fe_2O_3; these compounds form two series of solid solutions, one of ilmenite type and one of hematite type separated by a solubility gap which probably increases in size as the temperature falls(19).

Ilmenite is antiferromagnetic. Crystallographically its structure is derived from that of $Fe_2O_3\alpha$ by replacing every other layer of iron atoms by a layer of Ti atoms. These, in the ionic state Ti^{++++}, are not magnetic so that the alternations of the layers of cations can very probably be represented as: (+Fe) (Ti) (−Fe) (Ti) (+Fe) . . . where each layer is represented by brackets and the + and − signs represent the antiparallel orientations of the spontaneous magnetizations of the iron layers. In $Fe_2O_3\alpha$ the alternation is (+Fe) (−Fe) (+Fe) . . . .

Near the composition $Fe_{4/3}Ti_{2/3}O_3$ which is close to the limit of solid solution the compounds become definitely ferromagnetic with a molecular saturation moment of about $2\mu_B$. Such a large magnetic moment cannot be attributed to impurities or lattice defects but rather to a ferrimagnetic arrangement such as (+A) (−B) (+A) (−B) . . . in which the positive spontaneous magnetization of the A layers is a little greater than the negative one of the B layers. For instance, Nagata(20) suggests the compositions $(+Fe_{1/6}{}^{++}Fe_{2/3}{}^{+++}Ti_{1/6}{}^{++++})$ for the A layers and $(-Fe_{1/2}{}^{++}Ti_{1/2}{}^{++++})$ for the B layers giving a resultant molecular moment of $2\mu_B$.

§ 16. A POSSIBLE REVERSAL OF SPONTANEOUS MAGNETIZATION BY CHANGE OF COMPOSITION

As stated above, the solubility gap which exists around $m=0{\cdot}5$ probably becomes wider when the temperature becomes lower. Suppose that this process extends to the composition $Fe_{4/3}Ti_{2/3}O_3$: a new phase close to

Fe_2O_3 and very rich in iron will be formed at the expense of the original phase, which will then lose iron and gradually tend towards ilmenite in which the alternation of layers is (Fe^{++}) (Ti^{++++}) (Fe^{++}) . . . . This leads to an increase in the spontaneous magnetization of the A layers and a decrease in that of the B layers. At the beginning the magnetic alternation of layers is (+A) (−B) (+A) (−B) . . . and remains thus under the influence of the negative interactions between consecutive layers. But from the antiferromagnetic structure of ilmenite given above, there must also be negative interactions between the A layers. These negative interactions of AA type may become greater and greater as the spontaneous magnetization of A increases while on the other hand the AB interactions decrease with the decrease in spontaneous magnetization of B. A point would then be reached when the magnetic structure (+A) (−B) (+A) (−B) (+A) . . . with a positive *resultant* spontaneous magnetization, would become unstable and would invert to the more stable structure (+A) (−B) (−A) (−B) (+A) by reversal of the spontaneous magnetization of alternate A layers. This structure has *negative* resultant spontaneous magnetization. This reasoning presupposes that the spontaneous magnetization of the B layers maintains its original orientation despite both the reversal of some of the A layers and the thermal agitation. For this to be true it seems that there must be large enough positive interactions between B atoms in the same layer.

Whether this is true or not it is *a priori* not absurd that segregation of a solid solution into two phases during cooling could cause a reversal of T.R.M. by an atomic process involving negative molecular fields. It is evidently necessary to study the magnetic properties of compounds of the $Fe_{2-m}Ti_mO_3$ type carefully and to determine, preferably by neutron diffraction, the details of the antiferromagnetic structure and its modifications according to thermal treatment and change of concentration.

It will be seen later that exsolution can also give rise to a reversed T.R.M. by means of a demagnetizing field due to shape (cf. § 35).

SINGLE DOMAIN PARTICLES

§ 17. WALL THICKNESS AND GRAIN SIZE

In the range of magnetic fields in which hysteresis occurs, change of magnetization in ferromagnetic bodies is due to *rotation* of the spontaneous magnetization of the elementary domains and to *movement of the walls* separating them. In general the second process is more important in fields small compared with the coercive force.

The separating walls must not be regarded as infinitely thin surfaces but rather as zones of transition of finite thickness in which the magnetization gradually changes from the direction on one side to that on the other. The theory of these walls was put forward by F. Bloch⁽²¹⁾ and has since been developed by others⁽²²⁾: the *thickness* of the zone is given in order of magnitude by

$$p=a(NJ_s^2/K)^{1/2}$$

where a is the distance between neighbouring magnetic atoms, N the Weiss molecular field coefficient and K the magnetocrystalline anisotropy energy. This gives wall thicknesses of the order of a few hundred to a few thousand Angströms.

These results show immediately that very small grains of dimensions of the order of and less than p, can only contain a single domain since there is no space for a wall. In these very fine *single domain* grains, the magnetization is uniform and equal to the spontaneous magnetization J_s. The upper limit of grain size has been determined elsewhere (Néel(23)).

With such single domain grains changes of magnetization can only occur by the rotation process so that the phenomena are particularly simple.

As the ferromagnetic constituents of rocks are dispersed in very small grains it is natural to see how far their magnetic properties can be explained on the model of single-domain grains.

§ 18. ELEMENTARY MAGNETIZATION CYCLES(24)

In a single domain grain the internal magnetization energy depends only on the orientation of the magnetic moment with respect to certain axes in the grain. Considering, for simplification, magnetically uniaxial grains the energy E is given by

$$E = Kv \sin^2 \theta$$

where v is the volume of the grain and θ the angle between the magnetic moment and the axis.

The anisotropy constant K can arise in various ways. It can be due to a magnetocrystalline coupling so that K is equal to the anisotropy constant of a large crystal of the same material. It can arise from an anisotropy of shape : if the grain is an ellipsoid of revolution with demagnetizing field coefficients n along the axis and m in the equatorial plane, then

$$K = \tfrac{1}{2}\,(m - n)\,J_s^2.$$

Finally an anisotropy due to mechanical stress gives a value of K

$$K = \tfrac{3}{2}\lambda\sigma$$

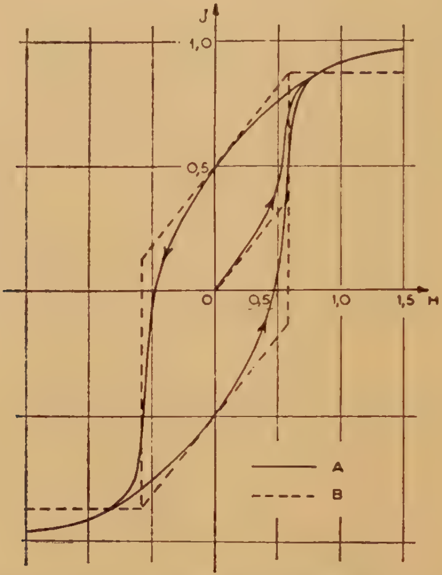
where σ is a tension parallel to the axis and λ is the longitudinal saturation magnetostriction of the material of the grain. The three mechanisms can of course act simultaneously.

In an actual system these would be a very large number of grains, oriented at random. But the properties of a grain depend greatly on its orientation with respect to the applied field.

When the axis of the ellipsoid is parallel to H, the hysteresis cycle is rectangular, with an overall height of $2J_s$ and overall width of $2H_c$. The coercive force H_c being given by $2K/J_s$. At $H = +H_c$ and $H = -H_c$ there are discontinuities in the magnetization, elsewhere the susceptibility is zero.

Conversely there is no hysteresis at all when the axis of the grain is perpendicular to the magnetic field. The component of the magnetic moment along the field is constant and equal to $v--J_s$ when $H<-H_c$, varies linearly from $-vJ_s$ to $+vJ_s$ as H changes from $--H_c$ to $+H_c$ and is constant at $+vJ_s$ when $H>+H_c$.

Fig. 3



Limiting hysteresis cycle and initial magnetization curve (full lines) for an assemblage of independent randomly oriented grains.

In a randomly oriented assemblage of independent grains, the average limiting cycle is$^{(25)}$ similar to fig. 3, with a remanent magnetization J_r equal to $\frac{1}{2}J_s$ and a coercive force of 0·96 K/J_s about half the maximum coercive force of the individual grains$^{(26)}$. The initial susceptibility is $J_s^2/3K$. The limiting hysteresis cycle is analogous to that of 'hard' magnetic materials (Alnico, Ticonal etc.) which are now used for good permanent magnets.

§ 19. OBJECTIONS TO THE INTERPRETATION OF THE MAGNETIC PROPERTIES OF ROCKS BY MEANS OF THE THEORY OF SINGLE DOMAIN GRAINS

It is now possible to interpret the magnetic properties of a rock as those of an assemblage of randomly oriented single domain grains.

First there is a rather theoretical fundamental objection. The grains of ferromagnetic minerals in rocks vary from one to several hundred microns in size. Now for magnetite the critical diameter should be about 0·02–0·03 μ and certainly less than 0·1 μ. This value should be reasonably accurate as an order of magnitude since the formula used to get it$^{(23)}$ gives results for iron which are confirmed by direct measurement of the grain size with X-rays or an electron microscope.

The second objection is more experimental and concerns the ratio of the remanent magnetization of a rock specimen to its saturation magnetization: it can be shown experimentally (§ 38) that this ratio is proportional to the coercive force, whereas the theory of single-domain grains predicts a constant value of $\frac{1}{2}$. Also, Nagata⁽²⁷⁾ has shown that the coercive force of rocks increases as the grain-size decreases while theoretically it should not depend on size after the single domain size is reached.

However, all these facts will later be found explicable in terms of multi-domain grains.

The above arguments are based on the experimental data for rocks with fairly low coercive forces of less than 1000 oe in which the magnetic constituents are magnetites or titanomagnetites. They do not apply to rocks with minerals of the ilmenite–hematite type which have far higher coercive forces sometimes of several thousand oersteds.

In these, as already mentioned, it is possible that the model of single-domain grains does correspond to the actual structure of the rock. To prove this definitely their magnetic properties must be more closely studied. Valuable information can be got in this way particularly from application of Rayleigh's relations.

§ 20. LORD RAYLEIGH'S RELATIONS AND SINGLE-DOMAIN PARTICLES

The Rayleigh relations concerned here are those applying to magnetization in fields very weak compared to the coercive force. A statement of these relations will be given later with an interpretation of them obtained by considering the macroscopic hysteresis cycle as the sum of a large number of unsymmetrical elementary cycles. Each unsymmetrical cycle will correspond with a point (a, b) in a plane where a and b are the lower and higher coercive forces (cf. § 44).

An assemblage of single domain grains does not obey the two Rayleigh relations. Each grain in fact has a *symmetrical* cycle, so that $a=-b$ and all the points representing elementary cycles lie on the second bisector of the plane (a, b). Thus although it is possible to satisfy the first of Rayleigh's relations by an appropriate density of representative points on 0δ, it is impossible to satisfy the second relation because on the returning branch of the hysteresis cycle when the field H decreases from its maximum H_m to zero, the magnetization J maintains its maximum value J_m and only begins to decrease when H becomes negative. See § 44 and figs. 13–16.

§ 21. THE ROLE OF MAGNETIC INTERACTION BETWEEN GRAINS

In principle this provides a method of deciding whether the independent grains are multi-domains or single domains by finding whether they do or do not obey Rayleigh's second relation.

But when single-domain grains are sufficiently close to each other interactions become important and the problem is somewhat altered. We have shown elsewhere ⁽²⁸⁾ that it is then convenient to distinguish different effects.

First, the magnetic shape anisotropy is decreased by proximity and the mean coercive force is thus decreased from H_c to $H_c(1-v)$ where v is the volume of ferromagnetic grains in unit volume.

Then there is a sort of Lorentz field to be considered equal to $\frac{4}{3}\pi J_m$ where J_m is the mean magnetization per unit volume ; it is a *magnetizing* field which makes the whole hysteresis cycle more upright.

Last but most important from the present point of view are the variations of the Lorentz field from its mean value from place to place. The interacting magnetic field h applied to a grain by its neighbours is different for each grain but remains constant in direction and intensity provided the external field is small. The effect is as if the representative point of the primitive cycle $(-a, a)$ became instead $(-a-h, a-h)$ thus representing an unsymmetrical cycle. The two Rayleigh relations are then automatically obeyed without the need for any special distribution of anisotropy of the elementary grains.

It is interesting$^{(28)}$ that when the grains are very close ($v=0{\cdot}5$) the ratio BH_c/A at 0·70 is similar to the value 0·42 for the same ratio given by the domain wall theory$^{(29)}$ when the walls are very close to each other. Similarly the values of coercive force given by the wall theory and by the theory of single-domain grains are about the same when the volume occupied by magnetic substance and the unoccupied volume are of the same order. Generally speaking the properties of very imperfect substances are treated equally well by the wall theory or by the theory of single domains very close to each other.

Usually the volume of ferromagnetic constituents in a rock is very small, of the order of a few per cent so that interactions are weak but not negligible compared with the earth's field. In fact it has been shown$^{(28)}$ that the root-mean-square of the fluctuating field is of the order of vJ_s. If $J_s=500$ and $v=0{\cdot}02$ this gives 10 oe. 2% of single-domain grains dispersed in a non-magnetic matrix should thus obey the two Rayleigh relations between -10 and $+10$ oe. If the coercive force were large, say several hundred or several thousand oersteds, the discrepancies from Rayleigh's relations outside this interval, -10 to $+10$ oe should be easy to detect and should give a conclusion as to whether or not single-domain grains were concerned.

The range of validity of Rayleigh's relations is much greater in more complicated structures such as in aggregates of grains where the total relative volume of the aggregates is small but within each aggregate the grains are very close to each other. The theory of interacting single-domain grains is then very useful as will be seen later (cf. § 32).

§ 22. THERMO-REMANENT AND ISOTHERMAL REMANENT MAGNETIZATION

Although the dimensions of ferromagnetic grains in igneous rocks are generally too large for the theory of single-domain grains to be applied and although it leads to some conclusions which do not agree with certain experimental facts it is still of great interest because of its simplicity and the fact that in some cases (such as $Fe_2O_3\alpha$) it is probably correct.

In particular it allows of a very simple interpretation of the *magnetization by heating* of rocks in general. This is the property by which a rock, heated above its Curie Point and cooled to room temperature in a magnetic field H small compared with the coercive force, acquires a *permanent* magnetization at ordinary temperatures called the *thermo-remanent magnetization* (T.R.M.) which has the following properties⁽³¹⁾. It is much greater and more stable than the *isothermal remanent magnetization* (I.R.M.) obtained by the classical process of applying the same field H and then removing it, at constant temperature. Sometimes the T.R.M. acquired in a given field can be hundreds of times greater than the I.R.M. produced by the same field. The negative field required to destroy the magnetization is much greater for a T.R.M. than for an I.R.M. when only a field about the same as or even less than the original magnetizing field is needed. Finally the I.R.M. due to a small field can be destroyed by heating to a quite moderate temperature while the corresponding T.R.M. is unaffected.

§ 23. OUTLINE INTERPRETATION OF T.R.M.⁽³²⁾

To obtain an approximate explanation of these properties consider an assemblage of single domain grains whose individual coercive forces are distributed between zero and an upper limit which is a little higher than the overall coercive force H_c ; H_c being large compared to the magnetizing field H.

The I.R.M. produced by the field H is exclusively due to the grains having a coercive force less than H and therefore magnetized irreversibly by this field. This I.R.M. is small since only a small proportion of the order of H/H_c of the grains are affected and evidently it can be destroyed by an opposing field of about the magnitude of H.

To understand the thermo-remanent case it must be remembered that the individual coercive forces of the grains are of the order of K/J_s and tend to zero at the Curie Point. This is an experimental fact explained theoretically by the variation of K as J_s^2 whether K is due to shape anisotropy or a magneto-crystalline anisotropy arising from interactions similar to the magnetic dipolar coupling : thus H_c varies as J_s and tends to zero at the Curie Point (cf. § 41 again). Therefore even a very small magnetic field will suffice, near the Curie Point, to magnetize irreversibly all the grains of the assemblage. As the temperature falls the intensity of the magnetization of the grains will increase proportionally to the spontaneous magnetization while the direction in each grain remains fixed. At room temperature a T.R.M. is thus produced which is equal to the maximum possible I.R.M. J_r. To produce J_r isothermally a magnetic field of the order of the maximum coercive force H_c would be necessary. Evidently such a T.R.M. will be much higher and much more stable than the I.R.M. acquired in the same field.

This reasoning succeeds in explaining some of the curious properties of the T.R.M. but unfortunately leads to the conclusion that it is independent of the field H applied during cooling and always equal to the maximum remanence J_r of the limiting hysteresis cycle. This does not agree with the experimental facts that in small fields the T.R.M. varies as H and in slightly higher fields as $H^{1/2}$ (cf. § 42). Some factor, possibly the thermal agitation, must have been neglected.

§ 24. THERMAL AGITATION IN A SINGLE-DOMAIN GRAIN(32)

The magnetic moment $v\,J_s$ of a single-domain grain such as those considered earlier (§§ 17 and 18) can, in the absence of any applied magnetic field, take up two orientations both of equal minimum energy : $\theta=0$ and $\theta=\pi$. Obviously if the height of the potential barrier between these two positions is very large compared with kT, thermal fluctuations cannot move the magnetic moment from one position to the other so that it remains always in the direction to which it was originally brought by a magnetic field. However since the height of this potential barrier is $v\,H_cJ_s/2$ a value of v can always be found, so small that its height is of the order of kT, in which case thermal fluctuations can cause the moment to change spontaneously from one position to the other.

In these conditions if a remanent moment M_0 is given to each grain of an assemblage of identical grains, it will tend to zero exponentially, thus

$$M_r=M_0 \exp\,(-t/\tau_0)$$

where τ_0 is the relaxation time of the grain.

§ 25. DETERMINATION OF THE RELAXATION TIME

This relaxation time depends on perturbing couples acting on the magnetic moment of the grain. When there are no such couples the only force acting on the moment is the classical couple due to the energy term $Kv\,\sin^2\theta$ which, since the atomic moments are analogous to gyroscopes, produces a continuous precession of the moment around the axis of symmetry of the grain, θ remaining constant. This is no longer true when there are perturbing couples in the equatorial plane capable of changing the polar angle θ and allowing the magnetic moment to cross the equatorial plane.

It seems that the most active of these perturbing couples arise from elastic deformations of the grain by thermal agitation. Because of these deformations the grain loses its spheroidal symmetry and takes up the shape of, for instance, a triaxial ellipsoid. This causes the appearance of a magneto-elastic couple and a transverse demagnetizing field both of which tend to turn the magnetic moment in a meridian plane. Boltzmann's principle gives the distribution in energy levels close to the equatorial plane. Using this and knowing the speed of precession due to the perturbing couples it is easy to calculate the number of moments $v\,J_s$ which cross the equatorial plane per second and hence find the relaxation time. Thus if we put

$$C=\frac{eH}{2m}\,|3G\lambda+DJ_s^2|\left[\frac{2v}{\pi GkT}\right]^{1/2}$$

then

$$\frac{1}{\tau_0}=C\exp\left\{-\frac{vH_cJ_s}{2kT}\right\}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e, m are the charge and mass of the electron, G the shear modulus and D a numerical constant depending on the shape of the grain equal to about 3.

Similar calculations can be applied to the case where there is an external magnetic field h, parallel to the axis of the grain. There are two relaxation times τ $(0, \pi)$ and τ $(\pi, 0)$ for movement from the position $\theta=0$ to $\theta=\pi$ and conversely. These are

$$\frac{1}{\tau(0,\pi)}=C\left(1+\frac{h}{H_c}\right)\left(1-\frac{h^2}{H_c^{\,2}}\right)^{1/2}\exp\left\{-\frac{vJ_s\,(H_c+h)^2}{2H_ckT}\right\},$$

$$\frac{1}{\tau(\pi,0)}=C\left(1-\frac{h}{H_c}\right)\left(1-\frac{h^2}{H_c^{\,2}}\right)^{1/2}\exp\left\{-\frac{vJ_s\,(H_c-h)^2}{2H_ckT}\right\}.$$

§ 26. CRITICAL DIAMETER : BLOCKING TEMPERATURE

It is interesting to apply formula (1) to grains of iron in which $H_c=1000$, $J_s=1700$, $e/m=1{\cdot}76\times10^7$, $\lambda=20\times10^{-6}$, $G=0{\cdot}77\times10^{12}$ and $k=1{\cdot}38\times10^{-16}$. This gives relaxation times τ_0 varying from 10^{-1} sec to 10^9 sec as v/T varies from $3{\cdot}2\times10^{-21}$ to $7{\cdot}0\times10^{-21}$. Thus at room temperature spheres of iron 160 Å in diameter can keep the initial magnetization indefinitely while spheres only a little smaller, of 120 Å diameter are demagnetized almost instantaneously, in less than 0·1 sec.

These figures show that at a given temperature there is a fairly well defined critical diameter D_T separating the grains into two groups.

Grains in the first group with diameters greater than D_T keep the initial orientation of the magnetic moments indefinitely in false equilibrium despite the action of any magnetic field h which is small vis-á-vis the normal coercive force H_c.

In the second group of grains with diameters less than D_T, thermodynamic equilibrium is reached almost instantaneously. In a small field h, parallel to the axis of the grain the only two possible positions for the moment are parallel or antiparallel to the field ; then the mean magnetic moment of the grain is given by

$$M(T)=vJ_s(T)th\frac{vhJ_s(\tau)}{kT}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The expression $J_s(T)$ is used to emphasize that J_s is a function of temperature. This moment $M(T)$ follows exactly any variations occurring in the applied field h.

The *blocking temperature* T_B is the temperature at which the diameter of the grain is the critical one or in other words the temperature at which the relaxation time becomes of the order of the duration of the experiments made on a rock. Thus in an *assemblage* of grains of very different volumes the blocking temperature can vary from the Curie Point for large grains to nearly absolute zero for very small grains.

§ 27. PROCESS OF ACQUIRING T.R.M.(32)

The process by which such an assemblage of grains acquires a T.R.M. can now be analysed. Consider the system cooled from above its Curie Point to room temperature in a weak magnetic field $h(T)$ which is a function of the temperature. At any temperature the grains of diameter D_T acquire a mean moment given by eqn. (2) with $h=h(T)$ and then keep this same moment as the temperature falls below T because the relaxation times become too long for the moment to change from one equilibrium position to the other. Strictly, taking account of the thermal variation of J_s the mean magnetic moment at room temperature $M(0)$ is

$$M(0)=vJ_s(0)th\frac{vJ_s(T)\,h(T)}{kT}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Thus at room temperature each grain has a mean magnetic moment which depends on the field $h(T)$ which was acting at the temperature T when the critical diameter became equal to the actual diameter of the grain. Hence the name blocking temperature.

The mean moment acquired in this way is not affected by chance variations in the field $h(0)$. On heating the system, thus magnetized, progressively in zero field the grains with blocking temperature T only lose their moment at T, that is at exactly the same temperature as they acquired this moment. As Thellier has put it, these grains have a magnetic memory and preserve the history of the magnetic field in which they cooled.

Equation (3) shows that the T.R.M. is proportional to the applied field h, when this is small enough.

Except for the small proportion acquired close to room temperature, the T.R.M. is particularly stable. In fact a field of the order of the coercive force of the grains, which may be very high, is needed to change it; similarly the relaxation time for spontaneous demagnetization is enormously long.

In contrast to this peculiar stability of T.R.M., an I.R.M. can be removed by an opposing field only about as great as that which produced it; in the same way the relaxation times are very much smaller than for a T.R.M. since the height of the potential barrier between the two stable positions of the magnetic moment is only of the order of $\frac{1}{2}vJ_sh$ instead of $\frac{1}{2}vJ_sH_c$.

§ 28. PARTIAL THERMO-REMANENT MAGNETIZATIONS (P.T.R.M.'s)

The properties ascribed by this theory to the T.R.M. of an assemblage of single-domain grains correspond remarkably well to the thermo-remanent properties of bricks and baked clays first described by Thellier(31) and to those of the rocks studied by Nagata(33). These properties have been well summarized by Thellier as follows(34): " To any temperature interval T_1, T_2 ($T_0<T_1<T_2<\theta$) there corresponds for a given specimen and a given magnetic field h, a particular magnetic moment which is acquired by the specimen when cooled from T_2 to T_1 in this field h. This moment is directed parallel to h and is unaffected by any heating to temperatures less than T_1 but disappears completely by heating to T_2. Further it is quite independent of other thermo-remanent moments acquired in temperature intervals outside T_1 and T_2 even though they be due to fields h that are different in magnitude and direction. All these moments are added geometrically but, paradoxical though it may seem, each is quite independent and preserves a sort of exact memory of the temperatures and field which produced it."

Can it be concluded from this agreement of theory and experiment that the ferromagnetic constituents of these specimens are single-domain grains? This is quite likely if the constituent is rhombohedral ferric oxide in which the ferromagnetic elements must be very small. But magnetites and titanomagnetites generally occur in grains of diameter much greater than a micron and the theory of single-domain grains cannot be applied to them. In addition, as will be shown later, the theory of large grains accounts for their properties much better than that of small grains. Thus it ought to be possible to explain the properties described by Thellier on other models than that of single domain grains (cf. § 57).

Thellier's(31) and Nagata's(33) experiments show that the blocking temperatures of magnetic rocks range from room temperature up to the Curie Point. But when there is only one ferromagnetic constituent, most of the T.R.M. is acquired in a fairly small temperature range about 50° below the Curie Point, so that for simplification each ferromagnetic constituent can be associated with a single blocking temperature.

§ 29. TIME-VARIATION OF ISOTHERMAL REMANENT MAGNETIZATION (I.R.M.)

Suppose that an assemblage of single-domain grains has been magnetized by a field H_m and that the remanent magnetization at time t_0 is σ_{r0}, the time origin being the instant at which the field H_m was removed. Roughly speaking, at time t_0 those grains with time constants τ less than t_0 will have lost their magnetization while those with $\tau > t_0$ will have kept theirs unchanged. Later at time t the remanent magnetization will have fallen to a lower value σ_r since grains with time constants between t_0 and t will have been demagnetized in their turn. Now the relation between the constants of a grain (v, H_c, . . . , etc.) and its relaxation time τ is

$$\frac{vH_cJ_s}{2k} = T_0(Q + \log \tau), \qquad . \ . \ . \ . \ . \ . \ . \quad (4)$$

where $Q = \log C$. Hence the decrease in remanent magnetization $\sigma_{r0} - \sigma_r$ must be proportional to the change in $T(Q + \log t)$ from t to t_0 provided this change is small, thus:

$$\sigma_r = \sigma_{r0} - AT_0(\log t - \log t_0). \qquad . \ . \ . \ . \ . \ . \quad (5)$$

The constant A depends on the distribution of the grains as a function of v and H_c.

Thus the decrease in remanent magnetization is proportional to the logarithm of the time. Some interesting results of Thellier's can be explained in this way ; in particular, for some specimens he found a logarithmic law for values of t from 20 sec to 5×10^6 sec. This decrease in remanent magnetization with time is only one of many aspects of the phenomenon of 'magnetic viscosity' shown by an assemblage of fine single-domain grains ; fuller details will be found in an earlier paper⁽³²⁾.

§ 30. THE EFFECT OF RISE OF TEMPERATURE ON REMANENT MAGNETIZATION

As above, let σ_{r0} be the remanent magnetization remaining at time t_0 at room temperature T_0, and suppose that the temperature is raised very quickly to T_1 and maintained constant at that level for a period of the same order as t_0. During this process $T(Q+\log t)$ increases by about $Q(T_1-T_0)$, producing demagnetization of a certain number of grains which remain demagnetized when the temperature is lowered again. A decrease of thermal origin has occurred in the spontaneous magnetization, given by

$$\sigma_r=\sigma_{r0}-AQ(T_1-T_0). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where A has the same value as above. The decrease in remanent magnetization is proportional to rise in temperature.

This phenomenon has been observed by Thellier⁽³¹⁾. From (5) and (6) one can obtain

$$\frac{\partial\sigma_r}{\partial\log t}\Big/\frac{\partial\sigma_r}{\partial T}=\frac{T_0}{Q}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The ratio of the two derivatives is equal to T_0/Q. Assuming reasonable values for the different parameters in the expression for Q one gets that Q varies from 19·9 to 23·4 as H_c varies from 10 to 10^4 oe. Taking the values $Q=22$ and $T=300°\text{K}$, T_0/Q is about 13·5. Thellier found for one specimen (No. C 25) the value 8·95.

Actually this argument is a little too simple because in the calculation of $\partial\sigma_r/\partial T$ the variations of H_c and J_s in eqn. (4) have been ignored. Both these decrease with rising temperature though exactly how is still poorly known. Therefore the decrease in σ_r with T is a little more than that calculated from eqn. (4) and the ratio of the two derivatives, equal to T_0/Q according to eqn. (7), is in fact a little less as in the experimental results.

§ 31. T.R.M. OF A MIXTURE OF TWO CONSTITUENTS⁽³⁵⁾

When there is a mixture of two ferromagnetic constituents A and B with clearly different Curie Points, the T.R.M. of the mixture sometimes has curious properties. As explained above (cf. § 26) the T.R.M. of constituent A is fixed at a blocking temperature T_a which is assumed here to be above the Curie Point of constituent B. Below T_a the T.R.M.

of A increases reversibly with the spontaneous magnetization of A as the temperature falls, independently of the applied field. But the T.R.M. of B is entirely dependent on the field acting on B at its own blocking temperature T_B. This field is the geometrical sum of the external applied field H and the demagnetizing field created by the previously magnetized grains of A. It can happen that this resultant field is opposite in direction to H and strong enough for the T.R.M. of B at room temperature to be greater than that of A. In these conditions, since the T.R.M. of B is negative, the total T.R.M. of the mixture is in the opposite sense to the field which caused it.

This phenomenon only occurs with a high concentration of ferromagnetic constituents. It certainly cannot happen if the grains of A and B are independently dispersed in a non-magnetic medium in the low proportions of a few per cent characteristic of igneous and sedimentary rocks. But it is the local proportions of A and B that matter, not the overall proportion in the rock. Negative T.R.M. can appear if the grains of A and B are *gathered in concentrated aggregates.* As the total concentration is small these aggregates must be far apart but that does not affect the issue.

The existence of such aggregates is not an artificial hypothesis : it amounts to saying that the two constituents have a common origin ; they could for instance have formed by exsolution into two phases, during slow cooling, of a homogeneous solid solution that was stable at higher temperatures, as must often occur in the system Fe_2O_3–TiO_2–FeO (cf. § 35). Furthermore such exsolution often gives rise to crystallites of very unsymmetrical shapes such as plates or rods which are, as will be explained later, favourable to the appearance of negative T.R.M.'s.

§ 32. REVERSED T.R.M. : SINGLE-DOMAIN GRAINS

The problem for single-domain grains has been discussed elsewhere by the author$^{(35)}$. The result is as follows for the simple case in which the concentrations of the two ferromagnetic constituents in the aggregate are both equal to $3c$. Suppose that the volume susceptibilities of the two constituents at their respective blocking temperatures are both equal to s, and that the magnetic grains are of elongated shape with a demagnetizing field coefficient of $\frac{4}{3}\pi - n$. Let R be the relative increase of spontaneous magnetization in each constituent from the blocking temperature to room temperature (the increase in the spontaneous magnetization of A from the blocking temperature T_B of B to room temperature is assumed negligible).

In these conditions it can be shown that the aggregates acquire a *negative T.R.M.* provided that

$$cnRs > \frac{2-8c+\frac{16}{3}c^2}{1-2c-2/R\,(1-3c)}. \qquad \ldots\ldots \quad (8)$$

Adopting the values $R=4$, $s=7$, $n=1{\cdot}7$ which the magnetic properties of rocks show to be reasonable, the inequality is satisfied if the concentration $3c$ of each of the constituents is greater than $0{\cdot}27$.

As $3c$ can vary from 0 to 0·5 it appears that negative T.R.M. is certainly possible in grains with properties similar to those of actual grains in ordinary lavas.

The inequality (8) also shows that negative thermo-remanence is favoured by a large anisotropy of the grains (n), by a large irreversible susceptibility (s) and by a high concentration of the two constituents (c). The Curie Points of A and B must also be far enough apart for the relative increase in spontaneous magnetization of A from T_a to T_b to be close to its final value R.

§ 33. REVERSED T.R.M. : LARGE GRAINS

The theory just summarized applies to single-domain grains but it is easy to show that aggregates of large grains could also develop negative T.R.M.'s. The argument depends only on the assumption that large grains have a blocking temperature ; this assumption will be proved later (cf. § 57). Consider a dense spherical aggregate composed of alternate layers of A and B, the thicknesses of the layers being equal and small compared to the radius of the aggregate ; each layer is equivalent to a large grain. At its blocking temperature T_a constituent A takes on a magnetization J_a such that the mean internal field of the aggregate is zero, hence

$$J_a=\frac{3H}{4\pi},$$

where H is the applied field. At the blocking temperature T_b of the second constituent the magnetization of A has increased to RJ_a, where R is the ratio of spontaneous magnetizations at T_b and T_a. The field within the aggregate which is the resultant of the applied field and the demagnetizing field of A is therefore $H(1-R)$. This is negative and must be compensated by the positive demagnetizing field due to a negative magnetization J_b of B given by

$$J_b=\frac{3H(1-R)}{4\pi}.$$

In this argument the reversible part of the susceptibility is neglected and the irreversible susceptibility of both constituents is assumed to be large compared to $3/4\pi$.

At room temperature the magnetizations of the two constituents become $R'RJ_a$ and $R''J_b$, R' and R'' being the relative increases of spontaneous magnetization for A and B respectively from T_b to room temperature. The mean T.R.M. J_{tr} of the whole aggregate at room temperature is therefore

$$J_{tr}=\frac{3H}{4\pi}\,(R'R+R''-RR'').$$

If the blocking temperatures T_a and T_b are sufficiently far apart R' will be close to 1, while if the magnetic properties of A and B are similar (except for the blocking temperatures) one can assume $R=R''$. The T.R.M. then has the sign of $(2-R)$ and is negative when the relative increase in spontaneous magnetization between the blocking temperature and room temperature is greater than 2.

This result is very similar to that for single domains. The inequality (8) shows that in fact that for $3c=0{\cdot}5$, R must be greater than $1{\cdot}5$ for there to be negative T.R.M. even if s is infinite.

§ 34. EXPERIMENTAL RESULTS ON THE REVERSED T.R.M. OF MIXTURES OF TWO CONSTITUENTS

Such phenomena as described above appear to have been experimentally observed by Nagata and his co-workers$^{(38)}$ in the dacitic lavas of Mt. Haruna and Mt. Asio, Japan. These rocks acquire a reversed thermoremanence in the laboratory and contain two distinct ferromagnetic constituents A and B separable by a magnetic extraction at a temperature between the two Curie Points. The constituent A with a Curie Point at about 500°c is a titanomagnetite spinel and has a magnetization curve very similar to that of magnetite. The B constituent having a Curie Point of about 200°c is a rhombohedral ferrimagnetic solid solution of ilmenite–hematite type and has a spontaneous magnetization which changes practically linearly with temperature all the way from absolute zero to the Curie Point. The magnetic properties of A and B are obviously very dissimilar so that the simplified theories given above are scarcely applicable. The concentration of B is extraordinarily small, only a few per cent of that of A. The fact that despite this the mixture acquires a reversed T.R.M. must be due to some peculiar capacity of B for acquiring a large T.R.M. This could be due to the high coercive force of rhombohedral lattices and also to the high values of R which are probably associated with the linear variation of spontaneous magnetization.

§ 35. REVERSED T.R.M. DUE TO EXSOLUTION

It is shown in § 32 that under certain conditions the shape demagnetizing field can produce a negative T.R.M. in a mixture of two constituents. It is there supposed that the two constituents exist before the thermal treatment in a magnetic field. But this condition is not absolutely necessary; as the following example shows a negative T.R.M. can also develop during a slow exsolution at room temperature.

Consider a spherical single-domain grain of a constituent A with spontaneous magnetization J_s and suppose that an exsolution occurs at room temperature precipitating a second magnetic phase B, accompanied of course by a change in composition of A. The first crystallites of the new phase B grow in the demagnetizing field of A, given by $\frac{4}{3}\pi J_s$. If the magnetocrystalline field of B is less than this, which it usually is, and if the exchange coupling between A and B is negligible the spontaneous magnetization of the crystallites of *B* will necessarily be oriented antiparallel to that of *A*. Further, once the process has started it will continue automatically during formation of phase *B* from phase *A*. This is true even if *A* disappears completely as in an allotropic transformation, when the final phase *B* would have a spontaneous magnetization opposite to that of the original *A* phase.

In an assemblage of grains of *A* having originally a mean T.R.M. in a particular direction, this process necessarily implies that as the *B* phase is precipitated the T.R.M. will decrease in intensity and, when the concentration of *B* is high enough, will change sign.

A detailed but more complicated analysis shows that similar, but perhaps less definite, phenomena can also occur in large multi-domain grains.

It should be noticed that this process of development of reversed T.R.M. is of great generality since it can accompany any allotropic transformation and any exsolution into two phases and does not depend on the relative positions of the Curie Points of the two phases. The ternary system TiO_2–Fe_2O_3–FeO which is of enormous geomagnetic importance, is particularly rich in the kind of transformation concerned. Not only are there solubility gaps at room temperature in the systems $Fe_{2-m}Ti_mO_3$ (Pouillard) and $Fe_{3-m}Ti_mO_4$ (Kawai, Kume and Sasajima) but also, according to Pouillard$^{(8)}$, intermediate compounds $Fe_{3-m-n}Ti_mO_{4-n}$ can exsolve into two phases each belonging to one of the first two series.

Besides these another process has been suggested by Graham$^{(37)}$ consisting of an alteration of constituent *A* to another constituent *B*, particularly oxidation of magnetite to maghemite; magnetically the process is very much as that described above.

Finally it is important to realise that the demagnetizing fields which cause these reversals are *local* demagnetizing fields, often of great intensity, related to the topography of the elementary domains. The exchange coupling between the crystallites of *A* and *B* has been neglected; this is reasonable when there is no crystallographic continuity between *A* and *B* but is doubtful if *B* is oriented in *A* by intergrowth. This exchange coupling, arising from the Weiss-Heisenberg forces can sometimes favour the development of reverse T.R.M. but more probably inhibits it. To say exactly what it does do, much more information is needed than is usually to hand, on the development and detailed structure of the precipitated phase. Thus negative T.R.M. by exsolution must be considered possible but not certain.

LARGE GRAINS

§ 36. VARIATION OF COERCIVE FORCE WITH GRAIN SIZE

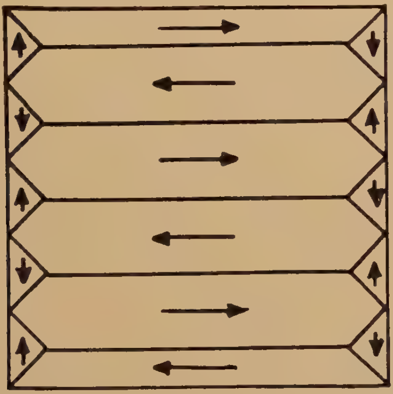
Generally speaking substances have a much smaller coercive force in the massive state than they have when finely divided in single-domain grains. The reason for this is that in the massive state the changes of magnetization in the hysteresis cycle are due to wall displacements, which in an unstrained and perfect substance require no expenditure of energy.

It can also be shown by experiment that as a massive substance is powdered into finer and finer grains, by physical or chemical means, the coercive force increases regularly and gradually tends towards the limiting value for single-domain grains$^{(38)}$. The coercive force is roughly speaking inversely proportional to the diameter p of the grains.

Although this result is extremely simple it has not yet been given any satisfactory explanation. The basic reason for this failure is that we have no precise idea at all of the mechanism of reversal of magnetization in medium-sized grains. Although Kittel proposed a mechanism some years ago$^{(39)}$ involving ‘ nucleation ’ of a phase magnetized antiparallel to the principal phase, quantitative application of his ideas gives results in complete disagreement with experiment.

Perhaps it is possible to suggest an approach which will give at the very most a lower limit to the coercive force of a large grain. During a complete hysteresis cycle the grain must twice pass through a state of zero total magnetic moment, corresponding to a particular subdivision of the grain into elementary domains. This state, with internal energy W (say), must be reached irreversibly so that the energy expended in single cycle, which is of the order of $2H_cJ_s$, must be at least $2W$.

Fig. 4



Subdivision of a cube into elementary domains giving zero total magnetic moment.

Consider a cube of side p of a magnetically uniaxial substance which has a magnetocrystalline energy, E_c, given by

$$E_c = K \sin^2 \theta,$$

where θ is the angle between the spontaneous magnetization J_s and the axis. In the demagnetized state the simplest domain system consists of elementary lamellar domains of thickness e completed, when K is small compared to J_s^2, by triangular closure domains (fig. 4). The corresponding energy is

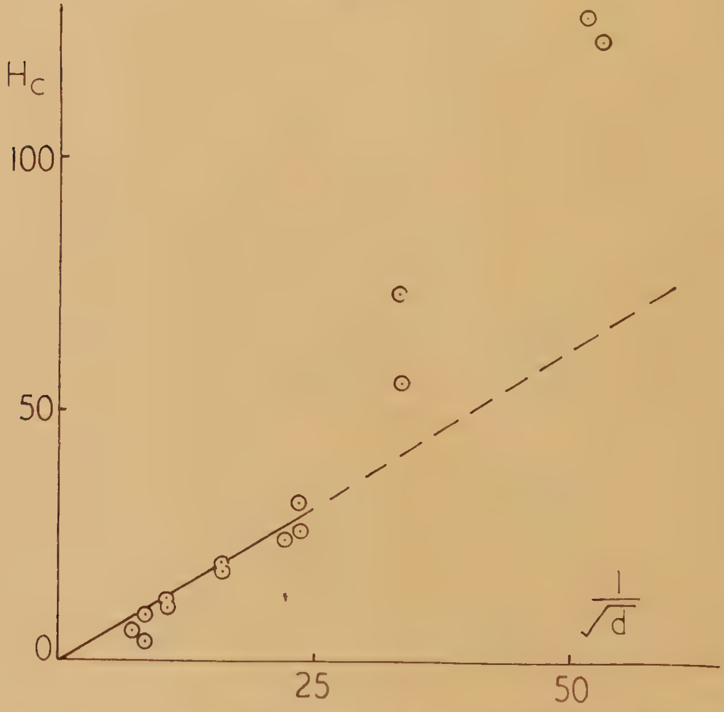
$$W=\frac{\gamma p^3}{e}+\tfrac{1}{2}Kep^2,$$

where γ is the wall surface energy. The thickness e takes the value at which this energy W is a minimum. Then equating H_cJ_s to this minimum value of W gives

$$H_c=\left(\frac{2K}{pJ_s^2}\right)^{1/2}. \qquad (9)$$

This formula has been applied to magnetite, assuming $K=10^5$ erg/cm^3, $\gamma=1$ erg/cm^2 and $J_s=450$, and the results compared with Gottschalk's$^{(38)}$ experimental results for powdered magnetite. Figure 5 shows that for p greater than 10^{-3} cm, eqn. (9) is in good agreement but that for smaller grains it gives too low a value for the coercive force.

Fig. 5



Coercive force of powdered magnetite as a function of $1/\sqrt{d}$, when d is the mean diameter of the grains. (Gottschalk's experimental results compared with the theoretical straight line given by formula (9).)

This discrepancy must be due to the difficulty of forming nuclei magnetized in the opposite direction to the principal phase. Since a demagnetizing field and a multiplicity of directions of easy magnetization favour the formation of such nuclei, the discrepancy from eqn. (9) should be very large in substances with only one direction of easy magnetization and with a demagnetizing field which is small compared to the magneto-crystalline fields. In fact for Mn–Bi which is such a substance, eqn. (9) gives coercive forces ten times smaller than those determined by Guillaud(40).

To summarize, it can be said that a satisfactory theory of the coercive force of large grains has still to be proposed.

§ 37. The Demagnetizing Field of Large Grains

The variation of coercive force H_c with the diameter p of the grain has just been described. Fundamentally this increase of coercive force derives from the fact that the size of the elementary domains becomes smaller as the grain becomes smaller. A similar increase occurs in a massive substance if a decrease in the size of the domains is produced by other means such as the formation of internal stresses varying irregularly on a small scale of distance. It is this decrease in domain size which causes an increase in the coercive force and therefore a general expansion of the hysteresis cycle along the H axis although the remanent magnetization is not changed and remains about half the saturation magnetization J_s.

In large grains another factor appears, the magnitude of the demagnetizing field. The demagnetizing field coefficient n is of the order of that for a sphere $4\pi/3$ and gives for an intensity of magnetization of 500 e.m.u. a considerable demagnetizing field of the order of 2000 oe. The effect of this can be simulated by ‘ inclining ’ the hysteresis cycle. This is done by using the same cycle and the same axis of magnetic fields in the (J, H) plane but a new sloping axis of intensity of magnetization with a gradient of $-1/n$.

The hysteresis cycle then appears flatter than the original cycle; in particular the remanent magnetization decreases and can be much less than half the coercive force. This characteristic property allows the presence of a demagnetizing field to be detected purely experimentally.

§ 38. Remanent Magnetization of an Assemblage of Large Grains

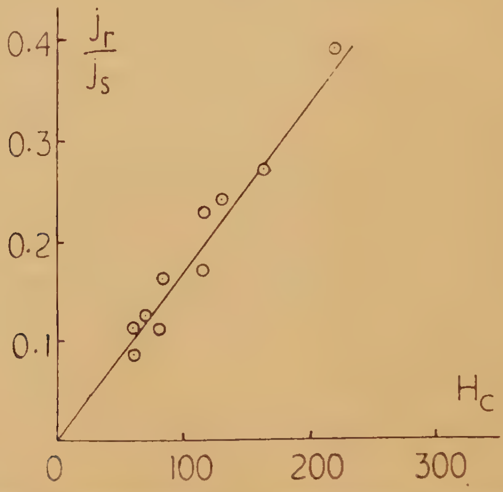
The remanent magnetization J_r of a large grain with a demagnetizing field coefficient n, after saturation in a field much higher than the coercive force, is given by the intersection of the descending branch of the limiting hysteresis cycle with a line of slope $1/n$ passing through the origin. If n is large the ordinate of the point of intersection is approximately equal to H_c/n. Then the ratio of the remanent to the saturation magnetization j_r/j_s is given by

$$\frac{j_r}{j_s}=\frac{H_c}{nJ_s}.$$

And, other things being equal, this ratio is proportional to the coercive force H_c.

Figure 6 constructed from data gathered by Nagata$^{(27)}$ for different rock specimens shows that this is approximately true. The experiment value of the constant of proportionality $1/nJ_s$ is about $\frac{1}{600}$. Assuming the average value of the saturation magnetization of the rocks given by Nagata$^{(27)}$ as 230 e.m.u. a mean value of 1/2·6 is got for $1/n$ which is very reasonable.

Fig. 6



The ratio of remanent magnetization j_r to saturation magnetization j_s plotted against coercive force for some eruptive rocks. (Nagata's experimental results compared with the straight line of formula (10).)

The approximation used above becomes inaccurate when j_r/j_s exceeds 0·3 since for high coercive forces it tends to a limiting value of 0·5. Amongst Nagata's data there can in fact be found two specimens with coercive forces of 465 oe and 345 oe and values of the j_r/j_s ratios J_r/J_s equal to 0·40 and 0·35 respectively. As expected they give points well below the straight line of fig. 6.

Thus the study of the remanent magnetization of rocks of low coercive force shows that the ferromagnetic constituents are in large grains and not in fine single-domain grains.

§ 39. Initial Susceptibility of an Assemblage of Large Grains

The apparent initial susceptibility of a ferromagnetic substance is strongly affected by the presence of a demagnetizing field (with coefficient n, say). Its apparent and real values, A' and A are related by

$$A' = \frac{A}{1+nA}.$$

When nA is large compared to 1 the apparent susceptibility A' is nearly equal to $1/n$.

In most magnetic substances A varies inversely as the coercive force and is about 0·2 when $H_c=500$ oe. For a sphere $1/n=0{\cdot}24$. Hence the apparent susceptibility of rocks with coercive forces of less than 500 oe, such as the eruptives studied by Nagata, must depend more on the demagnetizing field effects than on the intrinsic susceptibility of the material.

However ferromagnetic grains with very irregular shapes are better represented by triaxial ellipsoids than by spheres. The three demagnetizing coefficients along the three principal axes n_1, n_2 and n_3 are all different and

$$n_1+n_2+n_3=4\pi.$$

The apparent susceptibility of an aggregate of grains, *oriented at random* is then given by

$$A'=\frac{A}{3}\left(\frac{1}{1+An_1}+\frac{1}{1+An_2}+\frac{1}{1+An_3}\right).$$

It is easily shown that this is always greater than that of a sphere of the same material.

Obviously it will appear as if the demagnetizing coefficient n of the average grain is less than $\frac{4}{3}\pi$. Nagata, from an experimental study of the susceptibility of some igneous rocks, estimates that the average value of n is about 3·5 with $A'=0{\cdot}23$ and $A=0{\cdot}12$. With artificial mixtures of sand and large grains of powdered magnetite, n is found to be 3·15 when the susceptibility A of the same magnetite in the massive state is 0·43. The smaller value of A in natural specimens is probably connected with the higher value of their coercive force, which would imply a smaller value of A.

Thus the experimental results on the initial susceptibility of rocks are in excellent agreement with the large grain hypothesis. Though much less naturally explained by the theory of single-domain grains, they are not actually inconsistent with it.

§ 40. DISPLACEMENT OF A SINGLE WALL

To interpret the magnetic properties of large grains more fully it is necessary to consider the mechanism of the magnetization process. Wall displacements are, as stated above, the mechanism concerned. Consider the substance as composed of elementary domains which can be crossed from end to end by a wall.

The fundamental process is the movement of a single wall P (supposed plane) of surface-area S, its position being represented by the abscissa, z, of its intersection with an axis OZ perpendicular to the wall. This wall P separates two elementary domains with spontaneous magnetizations $+J_s$ and $-J_s$ and can move from $z=0$ to $z=L$, that is through a distance L which is called the *free path of the wall*. For $z=0$ the magnetic moment of the domain is $-LSJ_s$ and for $z=L$, $+LSJ_s$.

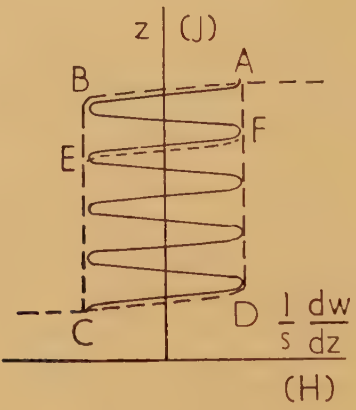
In a perfectly pure substance, the energy of the system W has a constant value W_0 in zero magnetic field, which is independent of the position z of the wall. In a field H, parallel to J, a pressure of $2HJ_s$ acts on the wall. An infinitely small positive field is enough to move the wall to its limit at $z=L$ and in infinitely small negative field brings it back to $z=0$. There is no hysteresis.

But in a real substance, which is always somewhat imperfect, W is a complicated function of z which varies haphazardly around the mean value W_0. With no applied field the wall is in equilibrium at points when W is a maximum. Application of a field H moves the wall until the equilibrium condition

$$2J_sH=\frac{1}{S}\frac{dW}{dz}$$

is satisfied. If the equilibrium is to be stable the second derivative d^2W/dz^2 must be positive. Thus to saturate the domain in the positive direction a field of at least the maximum value of $\frac{1}{2SJ_s}\frac{dW}{dz}$ must be applied. Therefore the coercive force depends on the maximum gradient of W.

Fig. 7



Hysteresis cycle given by a free path obstructed by equally spaced barriers all of the same height ; the full line represents the opposition, the broken one the hysteresis cycle.

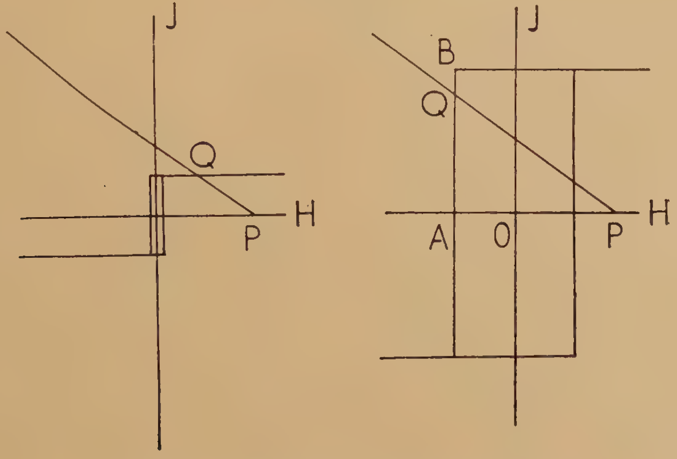
Lliboutry[(41)] gives a very suggestive graphical representation of these phenomena. He plots the quantity $(1/S)dW/dz$ which he calls the *opposition* as abscissa against the position z of the wall as ordinate. As stated above, z is proportional to the magnetization. This gives a curve C whose intersections, where its slope is positive, with the lines given by $x=2J_sH$ give points M corresponding to possible equilibrium states of the system. Except for certain volume changes, movements of M correspond to variations in magnetization with H.

The simplest model which has hysteresis, is obtained by representing the opposition as a sine curve A sin pz where p is large compared with $1/L$. This is the dotted line of fig. 7. The limiting hysteresis cycle ABCD (dashed line) approached a rectangle as p becomes greater. If at the point E on the vertical part of the return cycle the movement is stopped and the magnetic field increased again, the point representing the magnetization will follow the path EF which is nearly horizontal when p is large. For completeness it must be supposed that the coefficient A decreases as the temperature rises and tends to zero at the Curie Point.

§ 41. THERMO-REMANENT MAGNETIZATION OF THE MODEL WITH A SINGLE WALL

This model can be used to determine the thermo-remanent magnetization J_{tr} produced by cooling in a constant field H. It depends essentially on the mode of variation of the spontaneous magnetization J_s and the coercive force H_c with temperature, especially close to the Curie Point. Unfortunately experimental data on this are extremely scarce, while Forrer and Baffie$^{(42)}$ have shown that these phenomena are often very complicated.

Fig. 8



(*a*) (*b*)

The process of acquiring T.R.M. (see text).

Generally speaking theory and experiment agree that the true remanent magnetization J_r and the spontaneous magnetization J_s vary as $(\theta - T)^{1/2}$ in the neighbourhood of θ. But the form of the thermal variation of coercive force H_c is very different from one substance to another. This is not surprising since the coercive force is a complicated function of many independent factors. Forrer$^{(43)}$ found a variation of H_c with $(\theta - T)^{1/2}$ in large crystals of magnetite which had the low coercive force of 4 oe at room temperature, while for the very fine magnetite grains of a ferromagnetic rock with a very high coercive force Akimoto$^{(44)}$ found that H_c varied nearly as $(\theta - T)$.

Being concerned here with rocks of high coercive force such as these latter it seems better to use this last result. Then one has

$$\frac{H_c}{H_{c0}}=\left[\frac{J_s}{J_{s0}}\right]^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

H_{c0} and J_{s0} being the values of H_c and J_s at room temperature. The simplest form of hysteresis cycle is considered, as before ; a rectangular limiting cycle of height $2J_s$ and width $2H_c$ with all the partial cycles of the same width $2H_c$.

The demagnetizing field of the grain with a mean coefficient n plays an important part. Very close to the Curie Point the hysteresis cycle has the form of fig. 8 (*a*) and in an applied field $H=OP$ the magnetization is represented by the point of intersection Q, of a line of slope $-1/n$ through P, with the upper branch of the hysteresis cycle. As the temperature falls the cycle widens and takes the form of 8 (*b*) while the line PQ remains fixed, so that the point Q moves back along the upper branch of the cycle. It continues to move back as long as the ratio $r=AQ/AB$ continues to decrease. Now

$$r=\frac{H+H_c}{nJ_s}$$

and the derivative dr/dT vanishes when

$$\frac{dH_c}{dT}=\frac{H+H_c}{J_s}\frac{dJ_s}{dT}$$

or from eqn. (11) when $H=H_c$ and r has the value $n_0=2H/nJ_s$. From this temperature r increases as the temperature falls but Q the point representing the magnetization cannot move back up the descending part of the cycle BA. It describes (in reduced coordinates) a horizontal branch of the cycle of reduced height r_0.

At room temperature the specimen thus has a T.R.M. given by

$$J_{tr}=r_0J_{s0}.$$

It is not altered when H is removed and hence from eqn. (11)

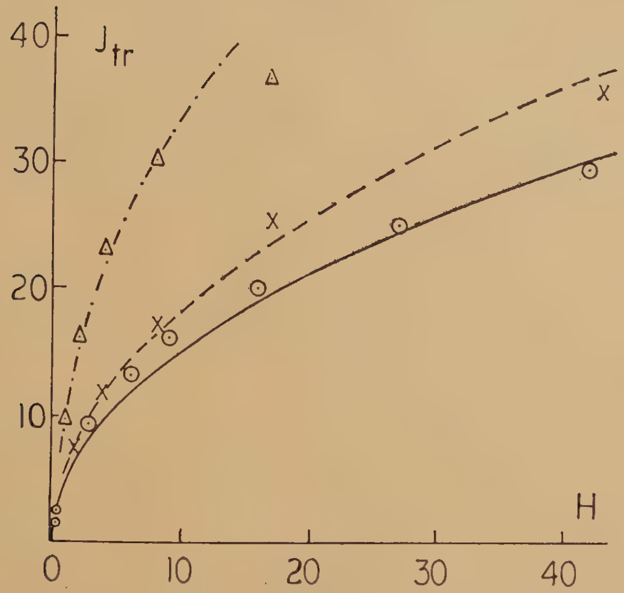
$$J_{tr}=\frac{2H^{1/2}\,H_{c0}{}^{1/2}}{n}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

The T.R.M. is thus proportional to the square root of the applied field and the square root of the coercive force.

§ 42. COMPARISON WITH EXPERIMENTAL RESULTS ; VALUE OF Q_k

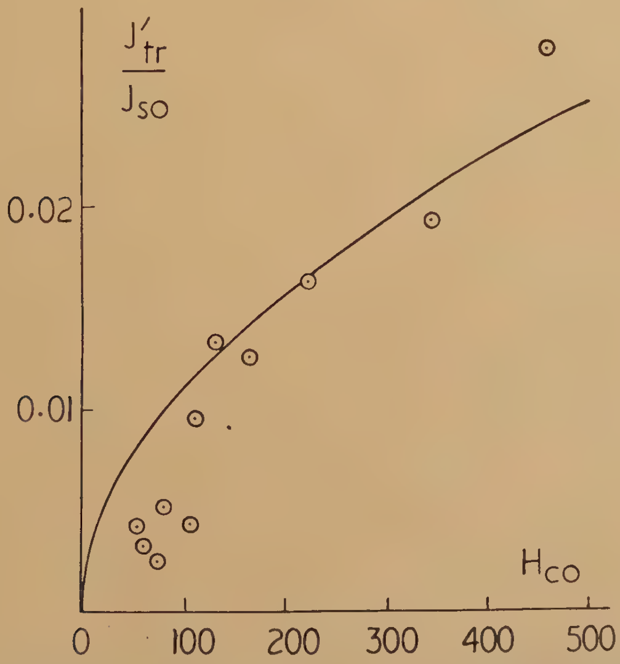
This theoretical formula is compared in fig. 9 with Nagata's(27) experimental results on a rock specimen (No. 60), with Mlle. Roquet's(45) results for a dispersion of fine grains ($\frac{1}{10}\,\mu$) of artificial magnetite in kaolin (M_2') and for artificial ferric oxide (F_5). In all cases the parabolic law represents the facts quite well, except in very low fields. This point will be considered later (§ 57).

Fig. 9



Variation of T.R.M. J_{tr} with the applied field H compared with the theoretical parabola (⊙=Spec. No. 60, Nagata; X=Spec. $M_2{}^1$, Mlle. Roquet; △=Spec. F_s).

Fig. 10



The ratio of T.R.M. in a field of 1 oe. $J_{t_r}{}^1$ to the saturation magnetization J_{s0} plotted against the coercive force H_{c0}. (Comparison of Nagata's results with the theoretical parabola of formula (12).)

Equation (12) shows that if J_{tr}^1 is the T.R.M. acquired in a field of 1 oe (Nagata's saturated T.R.M.) the ratio J_{tr}^1/J_{s0} should be equal to $2H_{c0}^{1/2}/nJ_{s0}$. Figure 10 shows the value of this ratio determined by Nagata for different specimens plotted against the value of H_{c0} and compared with the theoretical curve obtained with an assumed value of 1800 for nJ_{s0} (given by the theoretical values of $J_{s0}=450$ and $n=4{\cdot}19$).

Q_k is the ratio of T.R.M. in the earth's field Z to the magnetization induced by the same field. Since the induced magnetization is about Z/n

$$Q_k=2\left(\frac{H_c}{Z}\right)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

For $Z=0{\cdot}5$, Q_k should vary from 4 to 400 as H_c varies from 2 to 20 000 oersteds. Experiments do in fact show that Q_k is greater for rocks with a higher coercive force.

§ 43. STATEMENT OF LORD RAYLEIGH'S RELATIONS

The expressions for the magnetization of ferromagnetic bodies in *weak fields*, called Rayleigh's relations are particularly interesting in the case of rocks because the earth's magnetic field is always very weak compared to the coercive force of a rock.

Only a brief statement of them is necessary. The magnetization of a body, which has been previously demagnetized by an a.c. field gradually decreasing to zero, is a quadratic function of the applied field H :

$$J=AH+BH^2.$$

This is *Rayleigh's first relation.*

If, when the magnetic field has reached a value H_m, producing a magnetization J_m, it is reduced by an amount ΔH, the magnetization changes by ΔJ which has the same sign as ΔH and is given numerically by

$$|\Delta J|=A|\Delta H|+\tfrac{1}{2}B|\Delta H|^2.$$

This formula is only valid provided H remains inside the interval $-H_m$ to $+H_m$. Brown(47) calls this *Rayleigh's second relation*. The term of first order in H always has the form AH hence the coefficient A is called the reversible susceptibility.

From these formulae one can deduce that a magnetic field H_m leaves, when removed, a remanent magnetization J_r given by

$$J_r=\tfrac{1}{2}BH_m^2.$$

§ 44. THEORY OF RAYLEIGH'S RELATIONS

L. Néel(29) has shown that Rayleigh's relations can be explained on the single wall model. For this purpose a slightly more refined expression than that of § 40 must be used to represent the opposition $(1/S)dW/dz$. The curve of $(1/S)dW/dz$ is simulated by a series of straight lines A_1A_2,

A_2A_3, ... The projection of each section on the z-axis is the same and equal to $2l$ and the ordinates of the ends have a Gaussian random distribution about the mean value zero (fig. 11).

Fig. 11

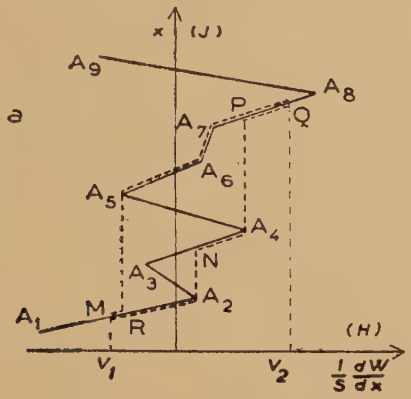
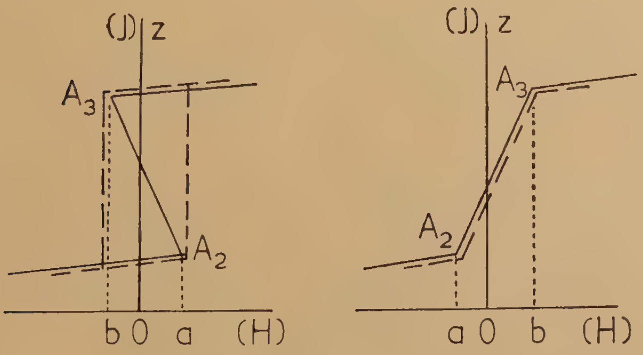


Diagram showing the course of a hysteresis cycle according to Lliboutry. The full line is the opposition and the broken one the hysteresis cycle.

In a field H_1 the wall is in equilibrium at the point M on the section A_1A_2 which has a positive slope (therefore stable equilibrium). The abscissa of M is $V_1 = 2H_1J_s = (1/S)dW/dz$. When the field is increased from H_1 to H_2 the point representing the position of the wall follows the path MA_2NA_4PQ with two discontinuities A_2—N and A_4—P; the return path is $QPA_7A_6A_5RM$ and hysteresis therefore occurs.

Fig. 12



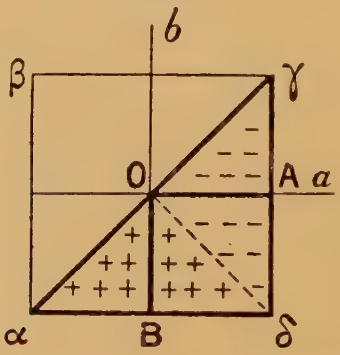
(*a*) (*b*)

(*a*) Irreversible and (*b*) reversible imaginary cycles corresponding to small wall displacements against an opposition represented by straight lines as in fig. 11.

In the range of weak fields these cycles reduce to the two imaginary elementary cycles of fig. 12, the first (*a*) representing the irreversible part of the phenomena and the second (*b*) the reversible part. If a and b are the critical fields corresponding to the abscissae of the points A_2 and A_3 each of the imaginary cycles can be represented by a point (a, b) in the plane Q of fig. 13. When there is a large number of walls, there will therefore be a large number of representative points whose density will be uniform close to O, the origin of coordinates in the plane Q.

The upper half of the plane (a, b) in which $a<b$ corresponds to AH the reversible term in the magnetization expression, the other half-plane where $a>b$ to the irreversible term in H^2. It was shown long ago by Weiss and Freudenreich(48) and later by Preisach(49) that an assembly of such unsymmetrical cycles corresponding to this second half-plane allows of an immediate explanation of Rayleigh's laws. According to these authors the cycles concerned were real ones such as those of isolated grains whereas in Néel's theory(29), here described briefly in a form due to Lliboutry(41), they are imaginary cycles corresponding to partial displacement of walls.

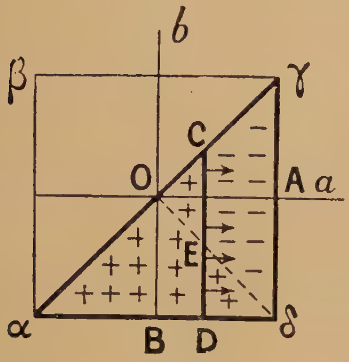
Fig. 13



The magnetic state of the imaginary irreversible cycles after demagnetization in a decreasing alternating field. After demagnetization by heating above the Curie Point, cycles in the quadrant BOA are magnetized at random, some positively and some negatively.

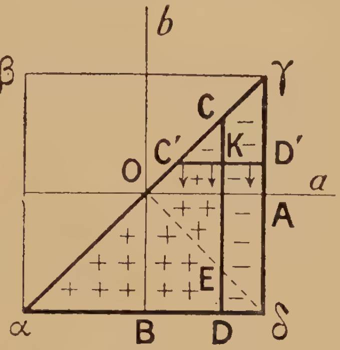
In zero applied field, the domains of the sector αOB (fig. 13) are always positively magnetized while those of sector AOγ are always negatively magnetized. But the domains of the quadrant BOA can have either sign according to the initial conditions. It is however easily shown that after demagnetization in a decreasing alternating field, the situation is as in fig. 13 when the domains are positively or negatively magnetized according as their representative points are below or above the second bisector Oδ. Application of an increasing field H causes reversal of the domains in the triangle OEC, the process being represented in fig. 14 where CD is a line with abscissa $a=H$. Similarly the return curve corresponds to the situation in fig. 15 where the abscissa of the line C′D′ is equal to the decreasing field. It is obvious without further argument that Rayleigh's two laws can be interpreted in this way.

Fig. 14



Magnetic state of the imaginary cycles during initial magnetization, after demagnetizing in decreasing a.c. field.

Fig. 15



Magnetic state of the imaginary cycles when the descending branch of the real hysteresis cycle is being followed.

§ 45. Demagnetization by Heating to above the Curie Point

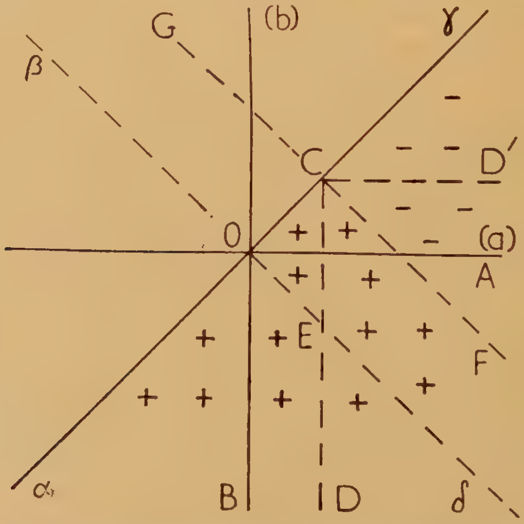
This demagnetizing process leads to a very different initial state from that produced in a decreasing alternating field. The two critical fields *a* and *b* of the imaginary cycles increase continuously from zero at the Curie Point to room temperature. There is no reason why the magnetization of these cycles should be of one sign rather than another so that in the limit the magnetizations of those in the quadrant BOA (fig. 13) are, after cooling, distributed at random. The result of this is that the initial magnetization curve of a thermally demagnetized body differs from the usual curve. The BH^2 term is smaller (since there are fewer domains to be reversed in the lower half of triangle OEC in fig. 14) and the AH term is larger since it must include terms due to reversal of a proportion of the domains of the trapezium BOED.

In this simple way Mlle. Roquet's interesting results, on the I.R.M. of artificial rocks, can be interpreted. She found⁽⁴⁵⁾ that the I.R.M. obtained after the first application of a field H is less than that produced after several cycles from $+H$ to $-H$. The difference between the two is roughly proportional to H for small fields while the I.R.M. obtained after several cycles ($\pm H$) is proportional to H^2 so that the phenomenon is more obvious when H is small. In the model outlined above the I.R.M. obtained after cyclical treatment corresponds as usual to the domains of the lower half of triangle OEC which remain positively magnetized. On the other hand the I.R.M. acquired after a single application of the field involves also the irreversible positive remagnetization of those domains in the area OBDE which have been left negatively magnetized by thermal demagnetization. During the next half-cycle this extra I.R.M. is compensated by one in the opposite direction due to another trapezium similar to OBDE but lying symmetrically on the other side of $O\gamma$; after completion of the cycle everything follows as before (see fig. 14).

§ 46. ANHYSTERETIC MAGNETIZATION

The higher values of anhysteretic magnetization as compared with the ordinary magnetization are also easily explained on this model. The anhysteretic magnetization is obtained by applying a field H and at the same time an alternating field which decreases to zero. It is easily shown that this will correspond to the positive magnetization of the domains of the area δEOCF whereas the ordinary magnetization produced by simple application of the same field H would be due only to those domains in the region COE (fig. 16).

Fig. 16



Magnetic state of the imaginary cycles after the action of a constant magnetic field together with a decreasing alternating one (the anhysteretic curve).

§ 47. THE REVERSIBLE TERM AND THE RATIO BH_c/A

Points in the plane (a, b) lying above the first bisector $\alpha\gamma$ correspond to reversible cycles such as in fig. 12 (b). In zero field the magnetic state is represented by all the domains below the second bisectrix 0β being positively magnetized and those above negatively. When a field H is applied the boundary between these two types domains moves from 0β to CG, when C is the point with abscissa $a \doteq H$. Thus the change in magnetization of the domains in this upper half of the plane represents the reversible AH term in Rayleigh's relations.

Theory shows⁽²⁹⁾ that the ratio BH_c/A should vary from 0·4 for substances in which $2l$ is of the order of L to about 1 when $2l$ is very small compared to L. It is found experimentally that it is about 0·5 in ' hard ' materials (such as used for permanent magnets) and up to several units in ' soft ' materials, in qualitative agreement with the theory. In rocks a value of about 0·5 should be expected since their ferromagnetic constituents tend to be ' hard '.

§ 48. THE EFFECT OF THE SHAPE DEMAGNETIZING FIELD ON RAYLEIGH'S RELATIONS

The form of Rayleigh's relations is not altered by the presence of a demagnetizing field. The initial magnetization relation is still expressed by an equation of the type

$$J = A'H + B'H^2$$

but the values of the coefficients are modified. If n is the demagnetizing coefficient it is easily shown that

$$A' = \frac{A}{1+nA}, \quad B' = \frac{B}{(1+nA)^3}.$$

It is also known that the presence of a demagnetizing field does not affect the apparent coercive force H_c' which remains equal to the real value H_c. Hence the relation between the apparent values A', B', H_c' and the real values A, B, H_c is

$$\frac{B'H_c'}{A'} = \frac{BH_c}{A} \frac{1}{(1+nA)^2}.$$

In magnetite A should be of the order 0·5—1 and for the grains found in rocks n is about 3 (cf. § 39). This means that the ratio $B'H_c/A'$ is probably 6–16 times smaller than the value of 0·5 found for BH_c/A in magnetically hard materials. This is a considerable decrease and provides a very good method for determining whether a material is composed of *large ferromagnetic grains* dispersed in a non-magnetic matrix. It does not seem to have been used yet.

MAGNETIC VISCOSITY IN LARGE GRAINS

§ 49. THE DIFFERENT TYPES OF MAGNETIC VISCOSITY⁽⁵⁰⁾

Time can play an important part in the phenomena of magnetization through a variety of effects.

The fundamental magnetic process, that is the alignment of an elementary atomic moment along a magnetic field, is itself not instantaneous. The magnetic moment undergoes a precession while its direction is moving into that of the applied field. However the duration of this process of alignment is very small, of the order of 10^{-10} sec ; it is only of importance in high frequency magnetic fields and so is of no interest in rock magnetism.

But *viscosity of diffusion* and *viscosity of thermal agitation* are important. The first is connected with diffusion of elementary material particles, atoms or electrons, within the crystal lattice. Obviously if the distribution of these particles depends on the orientation of the spontaneous magnetization relative to the crystallographic axes any change of magnetization must involve a non-instantaneous rearrangement of the particles. The example of carbon in the lattice of α-iron is the best known. The carbon atoms can occupy 3 different types of interstitial sites since each C atom has two diametrically opposite Fe neighbours, the line of whose centres can make different angles with the spontaneous magnetization and hence have different energies. At room temperature a time of about 1 min is required for a carbon atom to jump from one site to the next. The effect is easily observable since to reach a new equilibrium after a change in the direction of magnetization about the same amount of time is required.

Magnetite, with which we are particularly concerned, shows(52) a similar viscosity of diffusion due to movement of electrons from ferrous to ferric ions thus changing their valency. At 100°K these movements require times of about 1 min but at ordinary temperatures they are practically instantaneous and probably do not affect the normal processes of magnetization in rocks. Possibly other diffusion phenomena occur in the magnetic constituents of rocks at high temperatures but as there is no information whatever about them, the subject will not be discussed further, in spite of its great interest.

Generally speaking, viscosity of thermal agitation is due to irregular fluctuations in the forces acting on the spontaneous magnetization which enable it to cross barriers which it otherwise could not. In this way thermal agitation makes irreversible changes of magnetization possible and is an effect common to all ferromagnetic substances.

The effects of this viscosity on rotation processes have already been dealt with in a special application to single-domain particles. Its effects on wall movements must now be considered.

§ 50. THE VISCOSITY FIELD(50)

These effects can be described very simply by supposing that a fluctuating viscosity field $\pm H_f(t)$ is always added to the applied field H and that

$$H_f(t)=S(Q+\log t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where Q is a numerical constant of the order of 40 or 50, t is the time interval since the application of the field H and S, which has the dimensions of a magnetic field, is a constant characteristic of the specimen considered and dependent on the temperature.

In the absence of the viscosity field, we know that after a magnetic field H has given to a ferromagnetic substance a magnetization J_0, a small increase in the applied field of h produces a change in magnetization of j given by $j=(A+C)h$ while a small decrease gives a change

$$j'=-Ah.$$

A and C are the reversible and irreversible differential susceptibilities at the point (J_0, H) of the hysteresis cycle. With a fluctuating field the magnetization J after a time t is thus

$$J=J_0+C\,S(Q+\log t). \qquad (15)$$

Barbier's experiments[(53)] show that S has about the same value all round the hysteresis cycle.

§ 51. THE VISCOSITY OF FLUCTUATION IN THE RANGE RAYLEIGH'S RELATION

Formula (15) can be applied to some particular cases. In the Rayleigh region where the initial magnetization is given by

$$J=AH+BH^2$$

the irreversible differential susceptibility at the point (J, H) is $C=2\,BH$ as that including the viscosity term,

$$J=AH+BH^2+2\,BHS\,(Q+\log t). \qquad (16)$$

After application of a field H and then a return to zero field the remanent magnetization is $\frac{1}{2}BH^2$ and the irreversible susceptibility is $C=-BH$ so that the remanent magnetization after a lapse of time is

$$J_r=\tfrac{1}{2}BH^2-BHS\,(Q+\log t). \qquad (17)$$

This expression shows that the viscosity of isothermal remanent magnetization increases in relative importance with the size of the field which caused the magnetization.

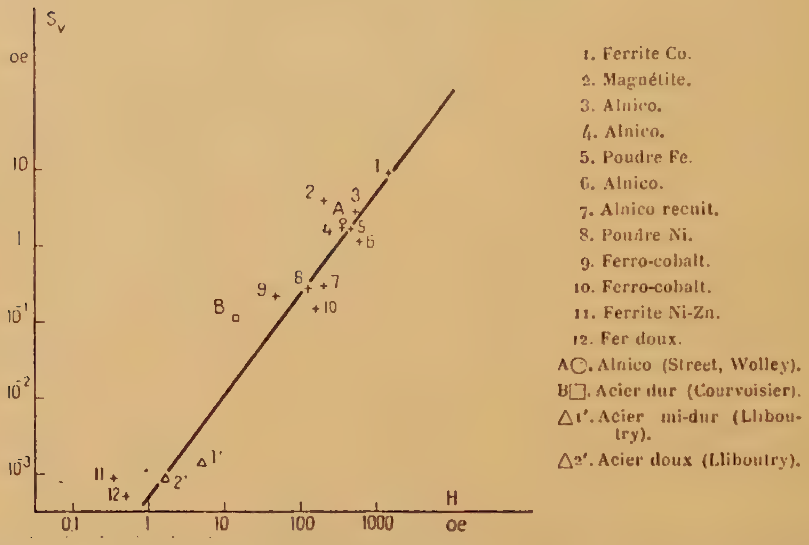
At different points of the limiting cycle, obtained after saturation in a very high field the magnitudes of the viscosity are greater in absolute value but less in relative value than in the preceding case. They can be calculated from formula (15) with $C=-k\,J_s/H_c$ where k is a numerical coefficient of about $\frac{1}{10}$ for $H=0$ (remanent magnetization) and several units for $H=H_c$, at which point the absolute value of the viscosity is a maximum.

§ 52. THE VALUES OF $S^{(53)}$

Barbier has made a thorough experimental study of these theoretical conclusions and shown them to be well founded.

He has also measured values of S for very diverse specimens and has found that S increases with the coercive force. Figure 17 summarizes his results and shows that S varies from about one thousandth of the coercive force for soft materials to about four thousandths for hard materials. These results are particularly interesting for they show that in substances with a coercive force of about 100 oersteds the viscosity field S log t is of the order of the earth's magnetic field.

Fig. 17



Values of the viscosity constant S for various specimens plotted against their coercive force (after J. C. Barbier).

§ 53. THEORETICAL CALCULATION(50) OF S

These thermal agitations may be considered to act through the mechanism of the internal dispersion fields produced by thermal oscillations of the spontaneous magnetization about its mean value. Suppose that the fluctuation field which helps a wall to cross an obstacle, that is to pass through a volume v (vJ_s corresponds to a Barkhausen discontinuity), is equal to the mean component H_m in a given direction of the dispersion field, over a similar volume v within an elementary domain. This mean value is a random function of time t whose mean square is given by equating the mean energy to kT. More exactly $H\rho$ the root mean square of H_m is

$$H\rho = \sqrt{\left(\frac{4\pi kT}{3v}\right)}.$$

Consider the possible values of H_m as having a Gaussian distribution and let θ be the reorganization time, that is the minimum time interval which must separate two observations in order that the corresponding values of H_m should be practically independent. In these conditions if ϵ is the probability that H_m is greater than a certain value H_f, a time $t=\theta/\epsilon$ must elapse for H_m to reach the value H_f with a probability of about 1. Then it is found that t is related to H_f by an expression of the type of (14), with the following values of Q and S :

$$Q \sim -2 \log \theta \, ; \; S = H\rho \, Q^{-1/2}.$$

The reorganization time θ is estimated to be of the order of 10^{-10} sec which gives values of Q of 40 to 50.

As Street and Woolley(54) have proposed, the thermal agitations can also be considered as affecting the heights of the barriers which oppose wall movements. If the fluctuations in the energy required to cross a barrier are of the order of kT the effects are the same as if the wall were acted on by a fluctuating field whose root mean square $H\rho$ was

$$H\rho = \frac{kT}{2J_s v}.$$

The argument then proceeds as before.

These considerations show that, if v is constant, S varies as $T^{1/2}$ if the thermal agitations are those of an internal dispersion field but as T if they are fluctuations in the heights of barriers. Barbier has studied the variations of S in a very wide temperature range and has found that in fact S varies approximately as $T^{3/4}$. Thus it seems probable that both the above mechanisms occur simultaneously but possible changes in v with temperature must also be considered.

§ 54. THE EFFECT OF THE DEMAGNETIZING FIELD ON VISCOSITY OF THERMAL AGITATION

To obtain expressions for magnetic viscosity in large grains the demagnetizing field must now be taken into account. The method used before (cf. § 37) can be employed for these calculations. In the Rayleigh region. where the term in H^2 is small compared to that in H, the initial magnetization relation, for instance, becomes

$$J = RAH + R^3BH^2 + 2R^3BHS\,(Q + \log t) \quad . \quad . \quad . \quad (18)$$

where the coefficient R is given by

$$R = \frac{1}{1 + nA},$$

n being the demagnetizing coefficient.

Similarly the remanent magnetization left after application and removal of a field H_m is

$$J_r = \tfrac{1}{2} R^3BH_m^{\,2} - R^3BH_mS(Q + \log t). \quad . \quad . \quad . \quad . \quad . \quad (19)$$

Thus in large grains as well as small grains the viscosity is proportional to log t agreeing with Thellier's experimental results(31). It is impossible to distinguish between the two cases from this point of view. The experimental facts on magnetic viscosity in rocks are also much too meagre to decide whether it varies with H_m as in (19). It would be equally interesting to know the values of S and whether they are related to H_c as in fig. 17.

Outside the Rayleigh region the effect of the demagnetizing field on the magnetic viscosity is more complicated. In particular when the irreversible susceptibility C becomes appreciable compared to the reversible susceptibility A the change of magnetization with time, J_t is given by

$$J_t = \frac{CS(Q+\log t)}{(1+nA)(1+nA+nC)}$$

which reduces, when C is large compared to A, to Barbier's(53) simple formula

$$J_t = \frac{CS(Q+\log t)}{(1+nC)}.$$

§ 55. THE EFFECT OF A RISE OF TEMPERATURE ON THE REMANENT MAGNETIZATION(50)

The arguments of § 53 show that the viscosity field

$$H_f = S(Q+\log t)$$

not only increases with time but also with temperature since S varies as $(T/v)^{1/2}$ or as T/vJ_s according to the mechanism involved.

Thus as well as an irreversible linear decrease in remanent magnetization with log t there should also be an irreversible decrease due to the rise in the viscosity field with temperature.

To observe this phenomenon it is necessary to exclude the reversible thermal variation in the principal term, $\frac{1}{2}R^3BH^2$, of J_r. To achieve this one takes advantage of the fact, predicted by Rayleigh's relations and confirmed by experiment, that a first order *decrease* in the viscosity field only produces a second order effect on the magnetization. Hence the fraction of the thermal variation of J_r due to the thermal increase of H_f can be obtained by determining the decrease in J_r produced by heating the specimen from T_0 to T_1 and then cooling to T_0 again.

However, it is not the increase in the viscosity field itself but the increase in the ratio of the viscosity field to the coercive force H_f/H_c that is important. In fact the walls have to cross barriers whose height decreases as the temperature rises and the coercive force is the measure of these heights. We are therefore concerned with the increase in the quantity

$$H_j' = H_{c0}S(Q+\log t)/H_c.$$

The phenomenon is found experimentally with about the predicted order of magnitude. Barbier(53) has studied it in ferromagnetic metal alloys and some artificial oxides with high coercive force. It has been observed by Thellier(31) and Mlle. Roquet(46) in baked clays and in dispersions of magnetite.

The ratio of the time variation to the thermal variation of remanent magnetization can be expressed quite simply. We have

$$\frac{\partial J_r}{\partial \log t} \Big/ \frac{\partial J_r}{\partial T} = \frac{\partial H_j'}{\partial \log t} \Big/ \frac{\partial H_j'}{\partial T}.$$

Simplifying the right-hand side by neglecting log t compared to Q and assuming the empirical variation of S with $T^{3/4}$ found by Barbier which lies between the two theoretical predictions, we get finally

$$\frac{\partial J_r}{\partial \log t} \bigg/ \frac{\partial J_r}{\partial T} = \frac{T}{Q}\left(\frac{3}{4} - \frac{\partial H_c}{\partial T}\right)^{-1}$$

in which all terms except Q can be determined experimentally. This gives a direct method of finding Q.

Assuming that Q is about 40 to 50 and neglecting the thermal change of coercive force, the formula predicts values of the ratio

$$\frac{\partial J_r}{\partial \log t} \bigg/ \frac{\partial J_r}{\partial T}$$

of the order of 8 to 10 at room temperature. Barbier has in fact found values of between 10 and 13 for magnetically hard materials which are exactly of the expected order of magnitude. Thellier(31) has found a ratio very close to 9 for a specimen of clay from Noron baked in nitrogen at 665°C. On the other hand Mlle. Roquet(46) in specimens containing mainly magnetite obtained ratios of 3·5 to 2·9. Possibly these low values are at least partly due to thermal variation of the coercive force. In fact from Forrer and Baffie's(42) experiments the value of $(T/H_c)\, \partial H_c/\partial T$ should be about $-0{\cdot}5$ which gives at $T=300°\text{K}$ and $Q=50$ a theoretical value equal to 4·8 of the ratio

$$\frac{\partial J_r}{\partial \log t} \bigg/ \frac{\partial J_r}{\partial T}.$$

The phenomenon dealt with in the next section may also be responsible.

§ 56. IRREVERSIBLE DECREASE OF REMANENT MAGNETIZATION DUE TO ANY CHANGE OF TEMPERATURE POSITIVE OR NEGATIVE

It is found experimentally that in certain relatively soft materials irreversible decreases of remanent magnetization may occur quite independently of those considered above, due to either *positive or negative* temperature changes. A mechanism entirely different in principle from the preceding ones must be concerned. It is probably a thermal change in the functions relating the energy of the system of walls to their positions in the crystal lattice. The result is an additional decrease of remanent magnetization with temperature and a decrease of the ratio $(\partial J_r/\partial \log t)/(\partial J_r/\partial T)$. In this way Barbier has found a ratio of 2·5 for a ferro-cobalt with a coercive force of 155 oe. The existence of this parasitic phenomenon is also revealed by the irreversible decrease of remanent magnetization J_r produced by cooling below room temperature and then allowing the temperature to rise again. This does not occur in the normal substances with which the original theory dealt.

Finally it should be noticed that thermal agitation produces analogous effects in both single domain and large grains; for instance in both, the same order of magnitude is found for the ratio of the decreases in I.R.M. due to time and due to rise in temperature.

§ 57. THERMO-REMANENT MAGNETIZATION IN VERY WEAK FIELDS

The brief theory of T.R.M. given earlier shows that it is proportional to $H^{1/2}$ (§ 41). In fact it is found experimentally that in very weak fields of about 1 oe it is more proportional to H than to $H^{1/2}$. The theory should not actually be valid for such small fields for no account has been taken of the thermal agitation field. In particular the blocking of walls probably cannot take place until the coercive force has reached a value at least equal to H_f, the thermal agitation field at temperatures near the Curie Point. In this region assuming the validity of (11), the spontaneous magnetization J is given by

$$\frac{H_f}{H_{c0}}=\left(\frac{J_s}{J_{s0}}\right)^2.$$

The magnetization acquired in a field H is then equal to H/n and assuming that the blocking occurs at this moment the T.R.M. at room temperature J_{tr}'' is given by multiplying again by J_{s0}/J_s:

$$J_{tr}''=\frac{H}{n}\left(\frac{H_{c0}}{H_f}\right)^{1/2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

This gives a proportionality to H in very small fields. From (12) and (20) J_{tr} should be equal to J_{tr}'' for $H=4H_f$ showing that the transition from one law to the other occurs for a field of 4 times the value of the fluctuation field at the Curie Point.

There are no experimental data to verify formula (20).

§ 58. THE ADDITIVITY OF PARTIAL T.R.M.S IN THE LARGE GRAIN MODEL

To what extent can the model of an assemblage of large grains account for Thellier's laws of the additivity of partial T.R.M.? It has already been shown (cf. §§ 27, 28) that all Thellier's laws are simply and naturally explained on the single domain model by the action of thermal agitation. Similar considerations will probably provide a start for attacking the problem in the large grain model.

Consider the free path L of a wall. A first approximation (§§ 40, 41) assumes the free path to be obstructed by a number of equally spaced barriers all of the same height; the second approximation, used in considering Rayleigh's relations (cf. §§ 44–46) supposes that the barriers are of different heights. Suppose now that the substance is acted on by a field H, small compared with the fluctuation field but large enough for the ratio vJ_sH/kT to be much greater than 1 (v is the volume through the wall passes in moving from one barrier to the next). In these conditions the possible crossing of the barrier depends on the magnitude of the fluctuation field compared to the height of the barrier.

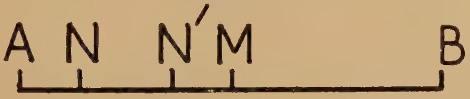
Consider a temperature T_1 less than the Curie Point θ and compare the total T.R.M. due to a field H with the partial T.R.M.'s acquired from θ to T_1 and from T_1 to room temperature in the same field. For this purpose the barriers are classed into two types: the first, A, including all barriers which can be crossed with the help of the thermal fluctuation field at temperatures below T; the second type, B, includes all the others, numbering q.

After demagnetization the wall lies, on the average, at the centre M of its free path AB(AB$=L$). If the field H acts continuously from θ to room temperature the wall crosses all the barriers and moves to the end A of its free path AB where it is found at room temperature definitely blocked. The path AM corresponds to the complete T.R.M.

If the field H acts only between θ and T_1, the wall again crosses all the barriers and reaches A, but after the field is removed at T_1 it can cross back over barriers of type A and is only stopped by those of type B. Thus on the average the wall is finally at a point N at a distance AN$=L/2q$ from A. The partial T.R.M. acquired between θ and T_1 is then proportional to the distance MN.

If H is applied only from T_1 to room temperature the wall remains at M on the average until T_1 is reached. After the field is applied at this point, it crosses all A-type barriers and stops when it meets the first of B type at N′ at a mean distance from M of $L/2q$. The partial T.R.M. from T to room temperature is then proportional to the distance MN′.

Fig. 18



Since NM+N′M=AM the total T.R.M. is equal to the sum of the two partial ones, and an important law of Thelliers is explained. The others can be derived similarly.

At first sight this argument seems to show that the different T.R.M.'s are independent of the field H. This is not true since in reality the free path AB must itself be considered as depending on H.

The whole argument is based on the assumption that the two types of barrier, high and low, are independent and that this distribution is not affected by temperature. It is no doubt a rough and ready mode of reasoning and could be improved, but it has the advantage of showing that it is possible to interpret Thellier's laws in the scheme of a theory of wall displacements.

Bibliography

(1) R. Becker and W. Döring, 1949, *Ferromagnetismus* (Berlin: Springer); R. M. Bozorth, 1951, *Ferromagnetism* (New York: Van Nostrand); L. F. Bates, 1951, *Modern Magnetism* (Cambridge: University Press); F. Pawlek, 1952, *Magnetische Werkstoffe* (Berlin: Springer); etc.

(2) L. Néel, 1948 a, *Ann. Phys.*, **3,** 137; 1948 b, *Ann. Inst. Fourier, Grenoble*, **1,** 163.

(3) T. F. W. Barth and E. Posnjak, 1932, *Z. Kristallogr.*, **82,** 325; E. J. W. Vervey and E. L. Heilmann, 1947, *J. Chem. Phys.*, **15,** 174.

(4) C. G. Shull *et al.*, 1951 a, *Phys. Rev.*, **83,** 208, 333; 1951 b, *Ibid.*, **84,** 912.

(5) F. C. Romeijn, 1953, *Philips Res. Rep.*, **8,** 304, 321.
(6) R. Pauthenet, 1952 a, *Thèse*, Grenoble ; 1952 b, *Ann. Phys.*, **7,** 710.
(7) E. W. Gorter, 1954 a, *Thesis*, Leiden ; 1954 b, *Philips Res. Rep.*, **9,** 295, 321, 403.
(8) A. Michel, 1937, *Ann. Chimie*, **8,** 317.
(9) N. Kawai, S. Kume and S. Sasajima, 1954, *Proc. Japan Acad.*, **7,** 588.
(10) L. Néel, 1932, *Ann. Phys.*, **17,** 5 ; 1934, *C.R. Acad. Sci., Paris*, **198,** 1311.
(11) M. Fallot and P. Maroni, 1951, *J. Phys. Rad.*, **12,** 253.
(12) C. Clark and W. Sucksmith, 1954, *Proc. Roy. Soc.* A, **225,** 147.
(13) H. Forestier and G. Guiot-Guillain, 1950, *C.R. Acad. Sci., Paris*, **230,** 1844 ; 1951, *Ibid.*, **232,** 1832 ; 1952, *Ibid.*, **235,** 48 ; 1953, *Ibid.*, **237,** 1554.
(14) R. Pauthenet and P. Blum, 1954, *C.R. Acad. Sci., Paris*, **239,** 33 ; G. Guiot-Guillain, R. Pauthenet and H. Forestier, 1954, *C.R. Acad. Sci., Paris*, **239,** 155.
(15) L. Néel, 1954, *C.R. Acad. Sci., Paris*, **239,** 8.
(16) Y. Yafet and C. Kittel, 1952, *Phys. Rev.*, **87,** 290.
(17) L. Néel, 1949, *Ann. Phys.*, **4,** 249.
(18) L. Néel and R. Pauthenet, 1952, *C.R. Acad. Sci., Paris*, **234,** 2172.
(19) R. Chevallier and J. Pierre, 1932, *Ann. Phys.*, **18,** 383 ; cf. ref. (8).
(20) T. Nagata, S. Akimoto and S. Uyeda, 1953, *J. Geomagn. Geoclectr.*, **5,** 168.
(21) F. Bloch, 1932, *Z. Phys.*, **74,** 295.
(22) L. Néel, 1944, *Cahiers de Phys.*, No. 25, p. 1.
(23) L. Néel, 1947, *C.R. Acad. Sci., Paris*, **224,** 1488.
(24) L. Néel, 1949, *Ann. Geophys.*, **5,** 99.
(25) E. C. Stoner and E. P. Wohlfarth, 1948, *Phil. Trans. Roy. Soc.* A, **240,** 599.
(26) L. Néel, 1947, *C.R. Acad. Sci., Paris*, **224,** 1550.
(27) T. Nagata, 1953, *Rock-Magnetism* (Tokyo : Maruzen).
(28) L. Néel, 1954, *Appl. Sci. Res., Hague*, B, **4,** 13.
(29) L. Néel, 1942, *Cahiers de Phys.*, No. 12, p. 1 ; 1943, *Ibid.*, No. 13, p. 18.
(30) L. Néel, 1946, *Ann. Univ. Grenoble*, **12,** 299.
(31) E. Thellier, 1938, *Ann. Inst. Phys. Globe*, **16,** 157 ; 1951, *J. Phys. Rad.*, **12,** 205.
(32) L. Néel, 1949, *Ann. Géophys.*, **5,** 99 ; cf. also ref. (17).
(33) T. Nagata, 1940, *Bull. Earthquake Res. Inst.*, **18,** 281 ; 1941 a, *Ibid.*, **19,** 49 ; 1941 b, *Ibid.*, **19,** 304 ; 1942, *Ibid.*, **20,** 192 ; 1943, *Ibid.*, **21,** 1.
(34) E. Thellier, 1946, *C.R. Acad. Sci., Paris*, **223,** 319.
(35) L. Néel, 1951, *Ann. Géophys.*, **7,** 90.
(36) T. Nagata, S. Uyeda and S. Akimoto, 1952, *J. Geomagn. Geoelectr.*, **4,** 22, 102 ; 1953, *Ibid.*, **5,** 168.
(37) J. W. Graham, 1953, *J. Geophys. Res.*, **58,** 243.
(38) V. Gottschalk, 1935, *Physics*, **6,** 127 ; V. Gottschalk and F. Wartman, 1935, *U.S. Bur. Mines, Rep. Investig.*, No. 3, 268, 67 and 83.
(39) C. Kittel, 1948, *Phys. Rev.*, **73,** 810.
(40) C. Guillaud, 1943, *Thèse*, Strasbourg.
(41) L. Lliboutry, 1951, *Ann. Phys.*, **6,** 731.
(42) R. Forrer and R. Baffie, 1944, *J. Phys. Rad.*, **5,** 97.
(43) R. Forrer, 1931, *J. Phys. Rad.*, **2,** 312.
(44) S. Akimoto, 1951, *J. Geomagn. Geoelectr.*, **3,** 47.
(45) J. Roquet, 1953, *Thèse*, Paris.
(46) Lord Rayleigh, 1887, *Phil. Mag.*, **23,** 225.
(47) W. F. Brown, 1949, *Phys. Rev.*, **75,** 147.
(48) P. Weiss and J. de Freudenreich, 1916, *Arch. Sc. Phys. Nat., Genève*, **42,** 449.

(49) F. Preisach, 1935, *Z. Phys.*, **94,** 277.
(50) L. Néel, 1950, *J. Phys. Rad.*, **11,** 49 ; 1951, *Ibid.*, **12,** 339 ; 1952, *Ibid.*, **13,** 249.
(51) J. L. Snoek, 1939, *Physica*, **6,** 161 ; 1941, *Ibid.*, **8,** 711 ; 1947, *New Developments in Ferromagnetic Materials* (Amsterdam : Elsevier).
(52) H. P. J. Wijn and H. van der Heide, 1953, *Rev. Mod. Phys.*, **25,** 98 ; H. P. J. Wijn, 1953, *Thesis*, Leiden.
(53) J. C. Barbier, 1954, *Ann. Phys.*, **9,** 84.
(54) R. Street and J. C. Woolley, 1949, *Proc. Phys. Soc.* A, **62,** 562 ; 1950, *Ibid.* B, **63,** 509 ; 1952, *Ibid.* B, **65,** 461, 679.

Rock Magnetism—Geophysical Aspects

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Summary

This review will not be concerned with rock magnetism as a geophysical tool to assist the geologist in unravelling structures and in the correlation of strata. No doubt the remarkable development since the war of the airborne magnetometer or fluxgate and the use in consequence now made of magnetic surveys will soon need to draw upon the increasing knowledge of the fundamental magnetic properties of rocks. Also the permanent magnetization of rocks varying in direction and intensity between strata will be an important assistance in the work of the geologist. However this review is solely concerned with the application of rock magnetism to the extension of our knowledge of the physical properties of the earth throughout geological time. An important stage in the development of our understanding of rock magnetism was the publication by Koenigsberger (1938) of an extensive review of work done up to that date in the field. Recently Nagata (1953) has reviewed very fully many aspects of the subject, particularly the method by which igneous rocks become magnetized and the physical properties of the iron oxide minerals responsible for the magnetization. This review will therefore be restricted mainly to the discussion of developments since Nagata's important book.

§ 1. Introduction

The magnetism of the rocks exposed at the earth's surface is dependent on the ferrimagnetic nature of certain of their accessory minerals. Except when these are absent, as in a pure limestone, the paramagnetism or diamagnetism of the common minerals such as quartz, felspar, calcite, etc. is too small to be of importance. Of the accessory minerals it is the opaque iron oxides which are of most interest. Their mode of occurrence in rocks is discussed in this number by Nicholls and their ferrimagnetic properties by Néel. Due to the dissemination of these in rocks a hand specimen has a remanent intensity of polarization $\mathbf{I}^r$ and a susceptibility k, which may vary, probably slightly, through the sample. If the rock sample is isotropic, the susceptibility k is a scalar, but often anisotropy is present to an important degree and then the susceptibility must be expressed as a symmetrical tensor. The induced moment per unit volume $\mathbf{I}^i$ in a field $\mathbf{H}$ is then

$$\mathbf{I}^i=[k]\,\mathbf{H}. \qquad (1)$$

By choosing a system of orthogonal axes x, y and z parallel to the three anisotropy axes of the sample the expression (1) reduces to

$$\left.\begin{aligned} I_x^i &= k_x H_x, \\ I_y^i &= k_y H_y, \\ I_z^i &= k_z H_z, \end{aligned}\right\} \qquad (2)$$

where k_x, k_y and k_z are the three principal values of susceptibility and the suffixes x, y, z denote the components of $\mathbf{I}^i$ and $\mathbf{H}$ along these axes. If k_x is the largest of the principal values, the x axis is known as the axis of easiest magnetization.

§ 2. MEASUREMENT OF PERMANENT MAGNETIZATION

The measurement of these quantities is not essentially difficult. The remanent magnetization of lava or other strongly magnetized rocks can even be quite accurately determined with a compass needle (see Rutten and de Boer (1954)). But in general it has to be done electromagnetically or with an astatic magnetometer. The former method has been developed mainly by the Department of Terrestrial Magnetism of the Carnegie Institution of Washington. Their pre-war instrument was described by E. A. Johnson and A. G. McNish (1938). A sample in the form of a cylinder 4 cm in diameter and 4 cm long is rotated at 10 cycles per second close to the centre of a pick-up coil. The intensity and phase of the alternating voltage in the coil is amplified and measured, giving the direction and intensity of the magnetization. It is possible with such an apparatus to detect an intensity of polarization of 2×10^{-8} gauss. Thus the direction of magnetization of samples having an intensity greater than 10^{-6} gauss could be determined to a degree. In 1950 an improved instrument was built in which the sensitivity was increased by a factor of 20 by rotating the sample in a lucite holder as a Beam's air turbine at 270 cycles per second.

The astatic magnetometer in studies of the susceptibility and permanent magnetization of rocks had been used by Japanese workers (see Nagata (1953)) and by Runcorn, Benson, Moore and Griffiths (1951). Recently a considerable improvement and elaboration has been made by Blackett (1952). Blackett shows that if the instrument is designed for the greatest ratio signal θ_H to thermal noise θ_0, then the sensitivity θ_H/H is given by

$$\frac{\theta_H}{H\theta_0} = \frac{T}{2\pi\epsilon^{1/2}}\frac{P}{I^{1/2}} \qquad (3)$$

where $\epsilon = kt$, k being Boltzmann's constant and t the temperature, P is the moment of either magnet, T is the time constant of the undamped system and I the moment of inertia of the magnet system, equal to αI_0 where I_0 is the moment of inertia of a single magnet and $\alpha > 2$. It is also possible to design for greatest sensitivity for a given period.

Then

$$\frac{\theta_H}{H} = \frac{T^2}{4\pi^2\alpha}\frac{P}{I_0}. \qquad (4)$$

Table 1 shows a comparison of the two designs of magnet system; those of Blackett are designed for highest signal to noise ratio, those of Creer for greatest sensitivity.

In order to remove the control arising from the geomagnetic field, the latter is compensated to about 1 part in a thousand by a system of Helmholtz coils and the effect of the residual field reduced by a high astaticism. Drifts of the suspended system are cut down by enclosing the instrument in a constant temperature enclosure and isolating it from vibration by mounting it on a separate foundation. The instrument responds to changes in the field gradient so difficulties arise during magnetic storms and when the instrument is not sufficiently removed from man-made disturbances or when the astaticism is poor.

Table 1. Typical Designs of Astatic Magnetometers

	Magnet material	Period sec	α	P	I	Field for 1 mm deflection at 5 m (gauss)	Minimum detectable field (gauss)
Blackett (1952)	Vectolite	25	4·5	60	0·037	$1{\cdot}2\times10^{-8}$	$2{\cdot}9\times10^{-10}$
Blackett (1952)	Alcomax IV	30	4·1	15	0·010	$1{\cdot}5\times10^{-8}$	$6{\cdot}7\times10^{-10}$
Creer (1955)	Alcomax IV	40	2·5	9·5	0·0044	$2{\cdot}4\times10^{-9}$	$2{\cdot}9\times10^{-10}$
Creer (1955)	Alcomax IV	15	2·5	9·5	0·0044	$1{\cdot}8\times10^{-8}$	$2{\cdot}9\times10^{-10}$
Creer (1955)	Ferroxdure	40	2·5	15·0	0·0044	$1{\cdot}8\times10^{-9}$	$2{\cdot}2\times10^{-10}$

The measurement of a permanent magnetization simply involves raising the specimen underneath the magnetometer and observing the deflections in different positions. The horizontal component is measured with the centre of the specimen vertically below the magnet system and the vertical component by displacing the centre of the specimen laterally from this position.

Considerable error in the determination of direction of magnetization of a rock specimen can arise if no allowance is made for the lack of uniformity in intensity of magnetization in it. This usually arises because the ferromagnetic minerals in rocks are not distributed uniformly. In calculations using the astatic magnetometer it has to be assumed that the resultant dipole is not quite at the centre of the specimen and to arrange the measurements so that the true direction of the dipole is obtained despite the effects which arise through it being off-centre.

An ingenious development of the astatic magnetometer is due to Kumagai and Kawai (1955) who rotate the specimen below an astatic magnetometer with a period of rotation equal to the period of free oscillation of the magnet system. At resonance the sensitivity is increased by a factor equal to the period divided by twice the damping factor.

§ 3. Measurement of Susceptibility

The susceptibility even if anisotropic can be measured with the astatic magnetometer by measuring the effect of imposing a small magnetic field on the specimen by means of Helmholtz coils. No systematic study of the anisotropy of susceptibility of rocks has been made, though Ising (1942) and Graham (1954 b) have done some measurements. It is a subject which deserves study as in general a proportion of iron oxide grains will be elongated or discoidal. By a number of mechanical processes these may be aligned in the rock and having an easy direction of magnetization may contribute a component of permanent magnetization not at all related to the magnetic field at the time of the formation of the rock.

§ 4. Considerations concerning the Choice of Rocks for Palaeomagnetic Investigations

The permanent magnetization of rocks in bulk, with which this review is concerned, has long been known to be caused in certain cases by the geomagnetic field at the time of the formation of the rocks, due to the physical, or possibly chemical, processes concerned therein. It has been known, mainly through the work of Koenigsberger (1938) and Nagata (1953), that in general the natural remanent magnetization of lavas, dykes and other igneous bodies, which have cooled from the molten state and therefore through the Curie point of their ferromagnetic constituents, possess a strong thermoremanent magnetization, the theory of which is considered in the article by Néel in this volume. The origin of the natural remanent magnetization of sediments is more obscure but in some cases at least it has been shown to be produced by the orienting effect of the geomagnetic field during deposition in lakes, rivers and the sea. The origin of the magnetization of metamorphic rocks in which considerable changes in mineral composition and texture have been induced by high temperatures and pressures is clearly more complicated and will not be discussed much in this review.

The geophysical aspect of rock magnetism is concerned with the broad knowledge of the behaviour of the geomagnetic field, which may be inferred from the study of the remanent magnetization of rocks of different ages and in different continents, and the interpretation of this in the light of our knowledge of the physics of the earth's interior. We might expect that this palaeomagnetic record was always incomplete and is perhaps now nearly obliterated. In some sediments and lavas the conditions at formation may not have been favourable for the acquisition of a uniform magnetization. In many rocks, chemical or physical changes in the iron oxide minerals due to diagenesis, may since their formation have caused considerable changes or the total loss of the original polarization. In some rocks the iron oxide minerals may through exposure to a field build up an isothermal remanent magnetization, also discussed in Néel's article, which will obscure, partially or totally, the original remanent magnetization. In many cases geological evidence will provide information relating to the first two pitfalls and evidence of magnetic instability may be obtained through laboratory tests. Nevertheless the ultimate test of whether the directions of magnetization measured in rocks are reliable indicators of the direction of the geomagnetic field at the time of their formation must lie in the self consistency of the field results themselves. No demonstration that the thermoremanent magnetization acquired by specimens of a lava cooling from the Curie point in the laboratory is similar to the natural magnetization of the lava flow in the field can determine the origin of the latter magnetization. Nor can the demonstration of magnetization under laboratory conditions provide proof of the origin of the remanent magnetization found in sedimentary strata in the field. To show however, in suitable instances, that the same direction of magnetization is observed in lava flows and sediments of the same geological age is to go far to demonstrate an origin in the geomagnetic field at the time of their formation. To show that sedimentary beds of the same age over the world have magnetizations consistent with a dipolar magnetic field is to show that local conditions cannot have influenced the remanent magnetization to any appreciable degree.

Consequently the only effective method of acquiring information about the behaviour of the geomagnetic field throughout geological time and also of understanding the origin and retention of the permanent magnetization of rocks is to compare field observations from different types of rock from different geological periods and from different parts of the world. In this review we will examine how far such a survey has progressed.

The study of palaeomagnetism would however be an entirely frustrating enterprise if no theoretical and empirical guides were available in the choice of rocks suitable for such purposes.

§ 5. STATISTICAL EXAMINATION OF DIRECTIONS OF MAGNETIZATION

If a number of samples are taken from one mass of rock such as a lava flow which may be expected to have been magnetized within a brief period such as a few years it is necessary to test the agreement of the measured directions of magnetizations by quantitative methods. Fisher (1953) has provided the necessary statistical method. The directions of magnetization may be considered as a cloud of points on a unit sphere, the stereographic or equal area projection of which is commonly used. The frequency of distribution of the points is given by $f=e^{\kappa c}$, where θ is the angular distance between a point and the true position, $c=\cos\theta$ and κ a measure of the precision. If there are N points and the resultant length R is obtained by adding vectorially the N unit vectors giving the N directions of magnetization, the probability distribution of the cosine of the angular error is

$$(N-1)\frac{(N-R)^{N-1}}{(N-Rc)^{N}}R\,dc$$

The probability P of a cosine less than c is

$$P=\left(\frac{N-R}{N-Rc}\right)^{N-1}-\ldots.$$

$$\therefore 1-c=\frac{N-R}{R}\left\{\left(\frac{1}{P}\right)^{\frac{1}{N-1}}-1\right\}.$$

This value of θ, which is termed the radius of the circle of confidence α, calculated from c for a given value of P gives a quantitative estimate of the precision of the mean value obtained from the N directions. We shall take $P=5\%$ throughout the review as being a degree of precision appropriate in the present stage of rock magnetism.

Of equal interest is a measure of the scatter within a set of observations which can be used to compare the scatter in different sets of observations. This is provided by the estimate $\hat{\kappa}$ of the statistic κ

$$\hat{\kappa}=\frac{N-1}{N-R}.$$

In measurements of the direction of magnetizations of single rock bodies the values of κ may vary from a few units (large scatter) to several hundred.

Cases in which undisturbed bodies of rock are found to be magnetized in a direction signficantly different from that of the present geomagnetic field provide *a priori* evidence of appreciable magnetic stability. Rock strata possessing this property invite first attention.

§ 6. FIELD TESTS OF STABILITY OF MAGNETIZATION

In an important paper Graham (1949) laid the basis for the examination of the magnetic stability of rocks by observing the relationship of direction of magnetization in different bodies of rock which have been disturbed in position since their formation.

Clearly in a lava which has cooled quickly or in sedimentary strata of nearly the same age we should expect the directions of magnetization to be nearly the same (allowing in the latter case for some scatter due to the geomagnetic secular variation), if the rocks are uncontorted and flat lying today. If the rock strata are tilted by different amounts in different places, the correction for geological dip should increase the value of κ, thus indicating a decrease in the scatter.

Graham pointed out the value of folded strata for this purpose and examined the method in a number of different formations. The basic aim behind the method is to test whether, after folding, any remagnetization has taken place. This might arise through heating to a moderate temperature by burial, resulting on cooling in the aquisition of a small but appreciable thermoremanent magnetization. Or it might more probably arise simply in the gaining of a component of isothermal remanent magnetization. In either case the new magnetization would be uniform in space and not related to the folded bedding planes. Thus after making correction for geological dip the scatter of the directions should decrease if the rock is magnetically stable and should increase if it is magnetically unstable. Graham applies the method to some folded Pleistocene varve clays at Middletown, Connecticut and shows that correction for tilt appreciably reduces the scatter of the direction of magnetization. He also demonstrates the stability of the Silurian Rose Hill formation of Pinto, Maryland, which was folded at the end of Palaeozoic times.

Graham applies a similar argument to conglomerate beds. These beds contain pebbles and fragments derived by erosion from sediments or lava flows. The present magnetizations, if the material has not been remagnetized, should be randomly directed. If the material has been completely remagnetized the magnetization of the separate pebbles should be nearly parallel. Graham was thus able to demonstrate the stability of consolidated fine-grained lake-deposits of the Ellensburg formation of Miocene age near Selah, Washington, which are magnetized generally in the direction of the present geomagnetic field. He is able to find near by lithologically similar material in the form of angular slabs in a conglomerate bed. He shows that while a number of them are uniformly magnetized, the directions of magnetization of different slabs are dispersed randomly in space.

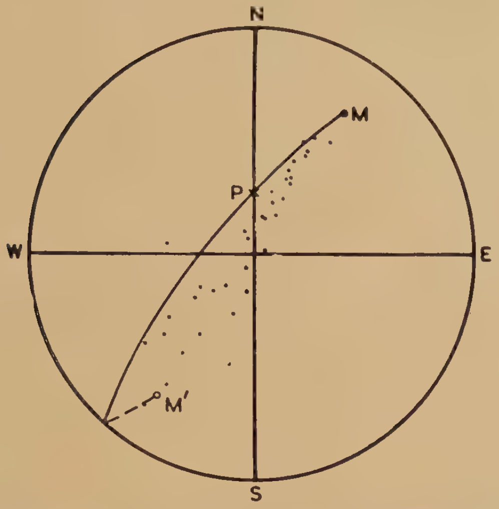
Graham's methods of testing the stability of magnetization are absolutely essential before it can safely be assumed that a rock formation possesses stability of magnetization to a sufficient degree for successful palaeomagnetic work.

§ 7. LABORATORY TESTS OF STABILITY OF MAGNETIZATION

Though the essential nature of such field tests is not in doubt, the development of simple laboratory tests to investigate which rocks are useful for palaeomagnetism is desirable.

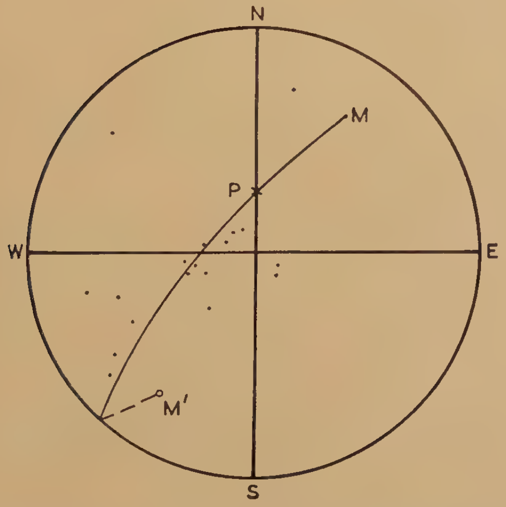
Kawai (1954) and Creer (1955) have made important developments in this field by examining rocks with partial stability. In many cases such partial stability results from the presence of an entirely stable and an unstable component of magnetization. Even in sediments the stable component may be thermoremanent in origin, being the residual of the magnetization acquired by the iron oxide minerals in the original igneous bodies from which the sediments have been derived. The unstable component must be isothermal remanent magnetization, possessing a logarithmic decay with time. Kawai (1954) has pointed out that these two components of magnetization in any one series of sediments are likely to be always the same in direction but of different magnitudes; thus the directions of magnetization of a number of specimens will lie on a great circle. Figures 1 and 2 show Creer's results on partially stable Triassic red sandstones from Beachley and Sidmouth. At the latter exposure Creer found a cliff the upper part of which has north–east declinations while the lower part has south–west declinations. A feature of the Triassic sediments of Great Britain discovered by Clegg, Almond and Stubbs (1954) is that

Fig. 1



Directions of magnetization of partially stable Keuper Marls from Sidmouth.
M, M′, averaged directions of magnetization of stable English Triassic rocks.
P, direction of geocentric axial dipole field.

Fig. 2



Directions of magnetization of partially stable Keuper rocks from Beachley.
M, M′, averaged directions of magnetization of stable English Triassic rocks.
P, direction of geocentric axial dipole field.

about half of the exposures they examined show a direction of magnetization N. 29° E. with a positive (downward) inclination of 34° and the rest an almost reversed direction of magnetization S. 39° W. with a negative (upward) inclination of 16°. These directions, with that of the present field, are shown on figs. 1 and 2. Creer interprets the scatter of the results at Beachley and Sidmouth in terms of the superposition on one or other of the two original magnetizations of a secondary unstable component along the present direction of the geomagnetic field.

We now proceed to survey according to geological age the results of the measurement of permanent magnetization of stable sediments and lava flows.

The rocks of Recent or Holocene times which have been investigated consist of two groups : lava flows which are post- or inter-glacial or which are dated historically and the varved clays of New England and Sweden which were deposited in glacial lakes.

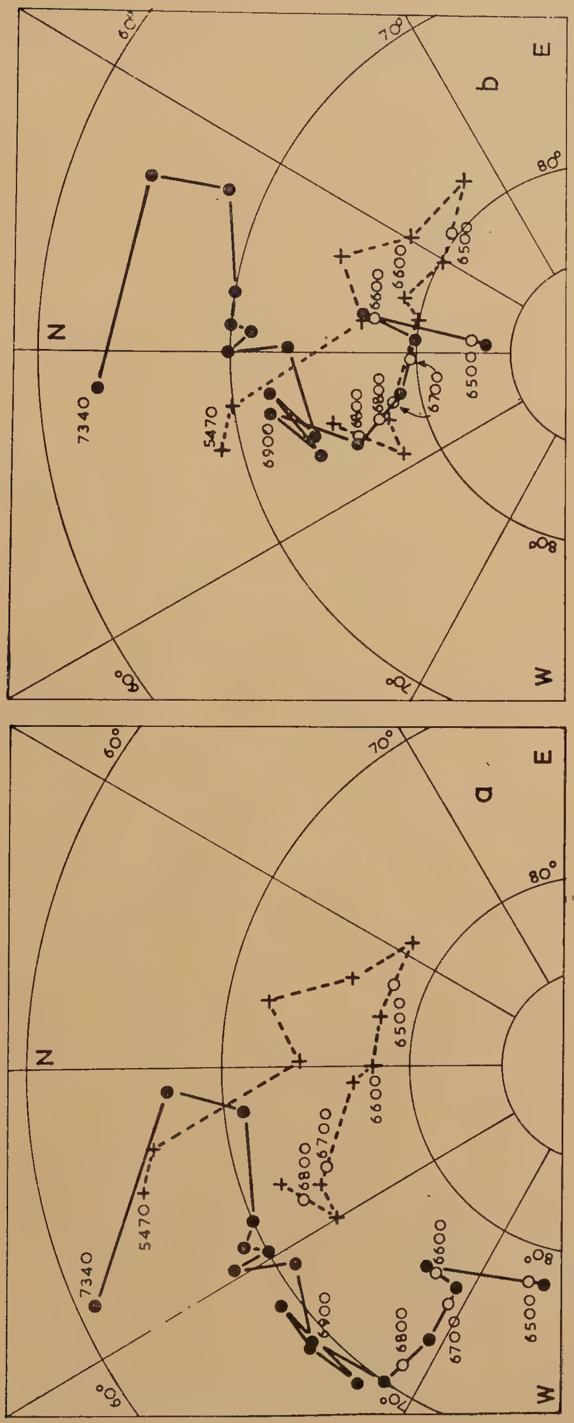
§ 8. PALAEOMAGNETISM OF THE HOLOCENE VARVED CLAYS

The varved clays of Sweden have been studied by Ising (1941), who in 1926 was the first scientist to investigate the possibility that sedimentary rocks might have become magnetized in the direction of the field in which they settled. On 350 years of varves from Viby, Sweden, Ising found the declination to be the same as that of the present day for the youngest and to differ by 10° for the oldest. The value of inclination found was 50° for the oldest and 30° for the youngest.

The study of the New England varved clays was taken up by McNish and Johnson (1938) and continued by Johnson, Murphy and Torreson (1948). In 5000 years of varves, the latest being dated by Urry at approximately 10 000 B.C., they found that the declination varied about due north by roughly ±30°. The inclination however was 65° for the youngest and 30° for the oldest.

Griffiths (1953, 1955) has carried out a detailed investigation of the varved clays of the Ångerman River in Sweden. Two localities, at Prästmon and Undrom, have been sampled ; measurements being made on samples each covering about 20 years of deposition. The varves may be correlated and dated, by the usual chronology, and the series at the two localities overlap between 150 B.C. and A.D. 250. Figure 3 shows the measured declination and inclination, each point representing the mean of five successive samples, i.e., 100 years. Griffiths shows that the reasonable agreement shown for the period of overlap depends on corrections being made for the geological dip of the beds (3° at Undrom but 11–13° at Prästmon). The radii of the circles of confidence for each point is 4° and the mean difference between the directions at the two localities during the period of overlap is 3° ; though if the dip correction had not

Fig. 3



Direction of remanent magnetization of Swedish Varved Clays (Griffith's data). (*a*) Uncorrected and (*b*) corrected for dip. Dates in years on Lidén's Time Scale where 7602 equals A.D. 1000. Prästmon ●; Undrom +; Interpolated points o.

been made this would have been 13°. This correction however assumes that the beds were horizontal at the time of deposition and magnetization, whereas the geological evidence points to the dip being the result of deposition in a delta.

Two cores of varved clays from the present delta of the Ångerman River near Kramfors, representing the period between A.D. 1300 and 1900, were examined and compared with the known changes of the geomagnetic field between A.D. 1500 and 1800. The results, though scattered, appeared to have the same trends as the known field changes, particularly a gradual change in declination from 20° E. in 1550 to 20° W. in 1750 which is known to have occurred. The varves of later date than A.D. 1800 give less consistent results than the earlier clays having a greater scatter with weaker polarizations. Griffiths finds the scatter in the recent delta deposits to be greater than those of the Prästmon and Undrom polarizations and postulates that the effect of river currents must be important in the process of magnetization. Griffiths has also found strong evidence for this in recent Icelandic varves, in which concordant magnetizations having no relation to the known field changes are found from localities 100 yards apart.

Tests of stability of the material are not easy because the original directions of magnetization are bound to be nearly coincident with the present field and the geological situation is such that Graham's methods cannot be used. Consequently Griffiths tested the varves for the presence of an appreciable component of isothermal remanent magnetization by remeasuring some of Prästmon samples after leaving them in the geomagnetic field in random orientations for over a year. No appreciable change in the direction of magnetization was noted. The natural remanent magnetization was not destroyed by 1000 gauss a.c. and although the varved clays could be magnetized in a field of 100 gauss this isothermal remanent magnetization could be removed by 100 gauss a.c. Thus it seems reasonable that the magnetizations of the iron oxide grains were thermoremanent in origin, the grains being orientated during deposition.

Because the varve clays are not consolidated they may easily be dispersed and the redeposition of such material under various controlled conditions in the laboratory therefore can throw light on the origin of the magnetization of sediments.

Johnson, Murphy and Graham (1948) examined the magnetization acquired on redeposition in low magnetic fields of dispersed varved clay from New England. They showed clearly that the declination acquired by the clay was accurately that of the ambient magnetic field but that the inclination was appreciably less. They interpreted their results by assuming that flat particles would tend to settle horizontally whatever the field direction was.

King (1955) has carried out further experiments of this kind on the Swedish varves, in which deposition takes place not only on to a horizontal surface but on one inclined at 10° to the horizontal. He concludes that the ferromagnetic grains are either flattened discs or spheres, the former of which will tend to settle horizontally onto the bedding plane. King determines for various inclinations (I_F) of the applied field values of the bedding error β and the inclination error δ. If I_0 is the inclination on the horizontal bed and I_{10} that when deposition takes place on the 10° slope then $\beta = I_{10} - I_0$ and $\delta = I_F - I_0$. Table 2 shows King's data on these two errors. From it is seen some experimental justification for Griffiths' correction for the geological dip of the beds in spite of the evidence that the beds had not been tilted.

Table 2. King's Data on the Bedding Errors and Inclination Errors of the Swedish Varved Clays

I_F	δ	β
0	2	8
10° N.	3	10
25° N.	9	8
45° N.	21	15
65° N.	27	17
90°	10	−25
80° S.	33	−17

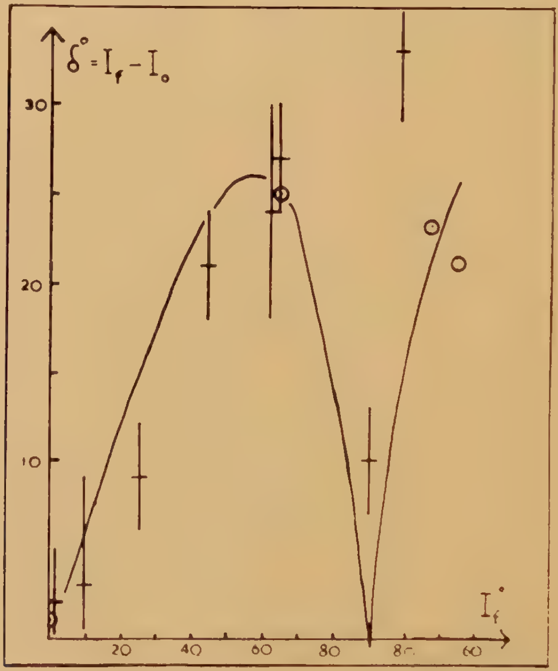
Assume that during deposition in the absence of appreciable movement in the fluid and the shear which results from this, the magnetic moments of the particles lie along the field. This seems almost certain to be true for small particles. Those particles which are not elongated or disc-shaped will consequently settle with their moments on the average along the field —some scatter will result from the process of settling in between the grains. Particles which are elongated or disc-shaped will settle predominantly with their long axes closer to the horizontal than the field. This will happen either on settling or during the first stages of compaction. We may infer from the experimental fact that the inclination of the polarization is generally less than that of the field that the elongated particles are magnetized along their length, which might be expected on physical grounds. We may also deduce that if the field is horizontal or vertical no error in inclination is to be expected, in the latter case because there is an equal probability that the particles will on settling rotate in either direction. These expectations are borne out by King's results in fig. 4. Now the simplest function connecting the angle of inclination (I_F) of the field and the resulting inclination (I_0) of the polarization of the sediment is the following :

$$\tan I_0 = f \tan I_F \qquad \ldots \ldots \ldots \quad (5)$$

where f is a factor less than 1 which is proportional to the fraction of the total grains which are round, and the probability with which flat grains take up a horizontal position on deposition. This relation, plotted in fig. 4, is seen to fit the data well.

Such experiments are of the greatest importance in investigating the origin of sedimentary magnetization, although it is not certain under what conditions the angle of inclination will be upset by such effects as described above. If the grains are predominantly flat it seems likely that compaction could also result in a decrease in the magnetic inclination. Compaction varies in amount very considerably with the lithology of the sediment—sandstones compact only by a few per cent but clays and shales by considerable amounts. Therefore one might especially expect errors in inclination in the latter. A comparison of the difference between the magnetic inclination in various lithologies is very much needed. It would be very interesting if the differences between similar lithologies depended on the palaeomagnetic inclination by eqn. (5).

Fig. 4



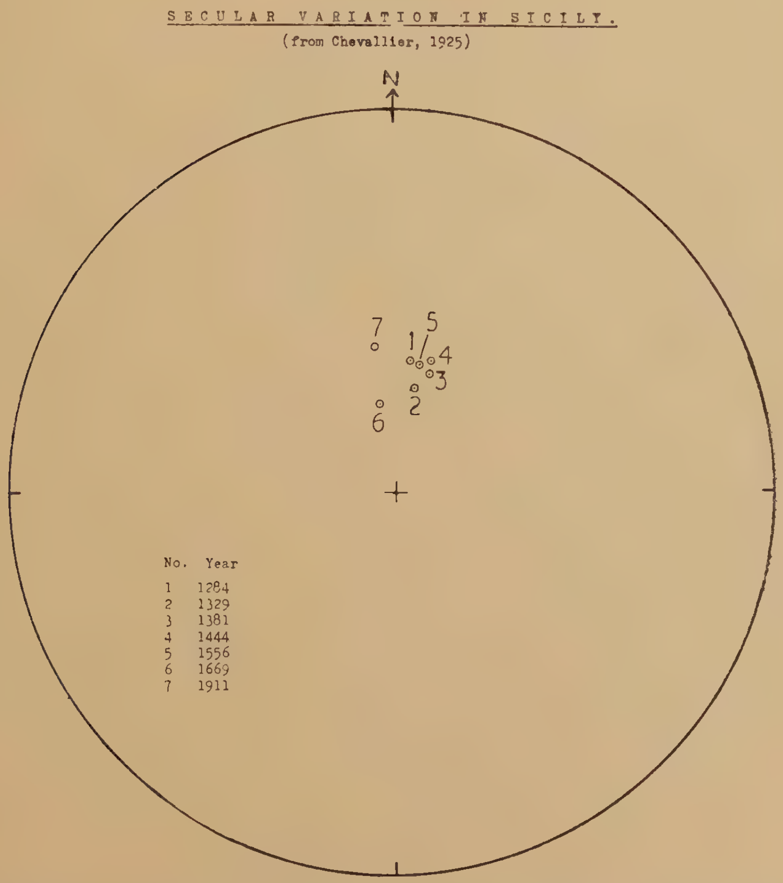
Inclination error in artificial deposition of Swedish Varved clays (King's data).

§ 9. PALAEOMAGNETISM OF QUATERNARY LAVA FLOWS (last million years)

Historic Flows

Chevallier (1925) carried out a thorough study of the permanent magnetization of the lava flows on Etna, the eruptions of which are dated. Figure 5 shows his results for declination and inclination drawn on a stereographic projection. Chevallier was able to show that the known secular variation of the geomagnetic field agrees with his results within about 2° from 1600 onwards. From fig. 5 it is seen that the curve traced out in space by the end of unit vector directed along the geomagnetic field show sa clockwise tendency. This is characteristic of all the extended records of the change of declination and inclination which we possess, and has been explained by Runcorn (to be published) in terms of the westward drift of the geomagnetic field.

Fig. 5



Stereogram of direction of magnetization of Etna lavas (Chevallier's data).

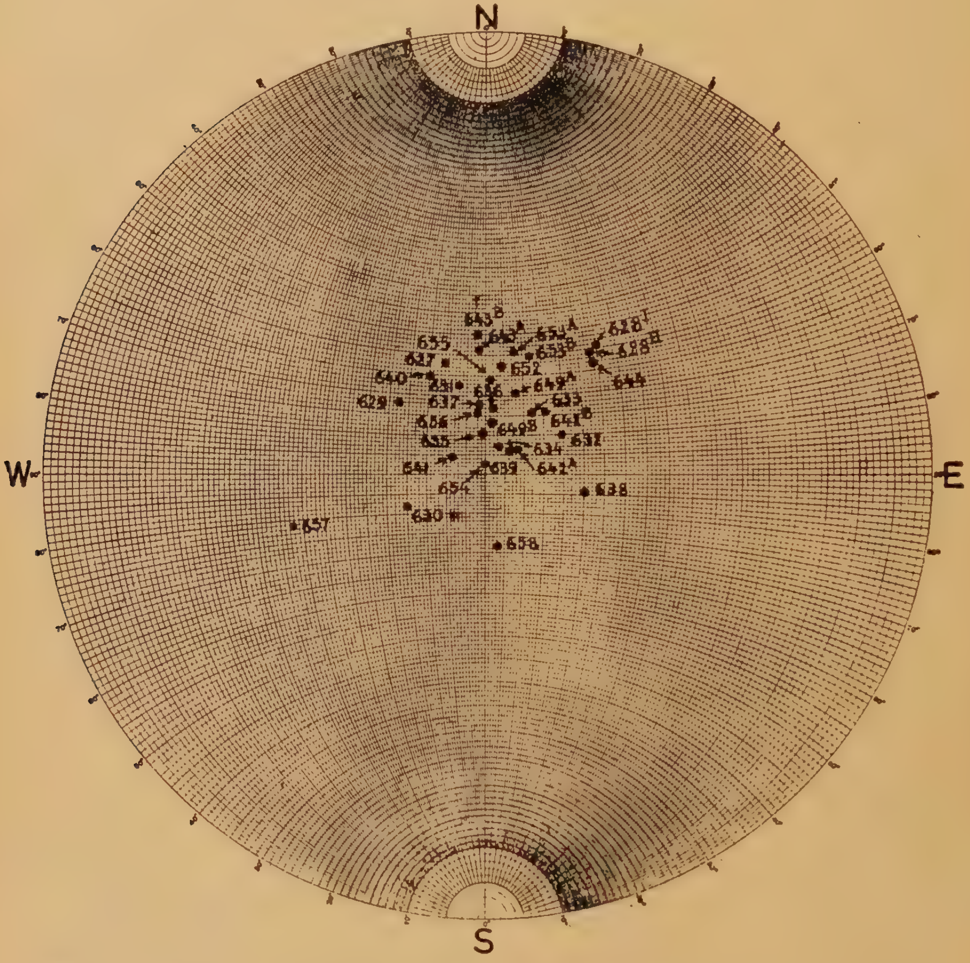
Hospers (1953) examined flows near Mt. Hekla in Iceland of A.D. 1766, 1845, 1878, 1913 and 1947–8 and a flow at Eldhraun N.E. of Lake Mývatn of date A.D. 1729. The directions of magnetization, calculated from measurements on 5, 4, 5, 3, 9 and 6 samples respectively from each flow, are given in fig. 6.

Minakami (1941) shows that the Yoridai-Sawa lava flow, which erupted on July 12, 1940 in Japan became magnetized in the direction of the local geomagnetic field.

Prehistoric Flows

In S.W. Iceland an average of four samples was measured by Hospers (1953) from each of eight flows younger than the end of the last ice age. He also measured a similar series from N. Iceland. Table 3 shows the mean directions for each series of flows.

Fig. 6



Stereogram of historic laval flows from Mt. Hekla, Iceland (Hospers' data).

Older Quaternary Flows

Hospers also showed that the Palagonite series of flows in Iceland, approximately 500 000 years old, are magnetized in the present direction of the geomagnetic field.

In W. and S.W. Iceland, an upper series of plateau basalts occur which are slightly different in appearance from the Tertiary flows below them and contain intercalated glacial beds resting (at Snaefellsnes) on an Early Quaternary sedimentary bed. Hospers (1954) therefore argues that these flows are early Quaternary in age. He shows (1953, 1954) that they are all reversely magnetized and this can not only be demonstrated at Snaefellsnes but in Hvalfjördhur and in Mt. Esja, 120 and 125 km away.

Table 3. Directions of Magnetization of Quaternary Lava Flows in Iceland

	Mean declination	Mean inclination	Angle with present field	Angle with dipole field	Radius of circle of confidence
Historic flows	N.4·3°E.	+76·2°	7°	1°	8·2°
Postglacial flows of S.W. Iceland	N.1·1°E.	+73·8°	7·5°	2·5°	8·2°
Postglacial flows of N. Iceland	N.67·0°E.	+86·4°	13·5°	11·5°	15·2°
Palagonite formation	N.7·1°E.	+75·5°	6·1°	2·0°	8·2°
Early Quaternary flows	N.181·0°E.	−75·2°	180°—6·3°	180°—1·5°	7°

§ 10. Palaeomagnetism of the Tertiary (1–70 million years)

At Snaefellsnes and in other sections in Iceland the underlying Tertiary basalts were found by Hospers (1951, 1953, 1954) to be magnetized in alternating zones of reversed and normal magnetization. Mean directions of these different groups are given in table 4.

Table 4. Mean Angle of Magnetization of Tertiary Lava Flows of Iceland

	Declination	Inclination	Angle of mean direction of magnetization with	
			present field	dipole field
Normal Tertiary W. Iceland			11·0°	12·0°
Reversed Tertiary W. Iceland			180°—16·0°	180°—13·6°
Normal Tertiary N. Iceland			6·2°	1·5°
Reversed Tertiary N. Iceland			180°—16·0°	180°—11·3°
Mean of Tertiary	N.1·5°E.	+77·8°		0·8°

The first example in the literature of a formation in Great Britain magnetized in a very different direction from that of the present geomagnetic field in spite of the rock being evidently in its original position occurs in magnetic surveys of the concealed Tertiary dykes in the Northumberland coalfield by Poole, Whetton and Taylor (1935). They were concerned with the applicability of magnetic methods of tracing these dykes, which are concealed from surface examination over long distances by glacial drift. They made traverses across the dykes with a Watts vertical force variometer. The Acklington dyke was examined in those localities at Broomhill, Swarland and Rothbury. Twenty-one, eighteen and eight 200–400 ft. traverses were made at these three localities respectively at intervals along the dyke between 200 and 2000 ft. Seven traverses of 1500 ft. of the dyke at Broomhill gave pronounced negative anomalies up to 400 γ in intensity, indicating that the magnetization was equivalent to a strong concentration of N. poles on the upper surface. About half the traverses of the Rothbury section and a third of the Swarland section also give rise to negative anomalies. The authors also found the Coley Hill dyke to give rise to negative anomalies. Rejecting the geometry of the dyke as a possible cause, the authors inferred tentatively that the weathering of the surface of the dyke was a possible cause of its inverse magnetization. A very striking case of such anomalous magnet W inverse magnetization. A very striking case of such anomalous magnetization was found by Gelletich (1937), who showed that the Pilansberg dyke system of South Africa was largely magnetized in a direction opposite to that of the present field. This great system of volcanic dykes extending over a distance 300 km long and 150 km wide is Palaeozoic or Pre-Cambrian in age and it is convenient to discuss the detailed results later in the article.

Bruckshaw and Robertson (1949) have examined in detail three of the Tholeiite dykes of North England and they showed them to be in general reversely magnetized at a number of places along their length in nearly the opposite direction to the field of the present day. They were among the first to point out that such magnetization must have been caused by the presence of an inverted magnetic field but left open the possibility that it arose quite locally. They found some sections of the dykes to be normally magnetized but noticed that these specimens when left in the laboratory for some months changed their directions of magnetization considerably. It seems clear now that these specimens possessed isothermal remanent magnetization. More difficult to understand is that Bruckshaw and Robertson found that the dykes were in general not uniformly magnetized but were scattered in direction very much as if a certain amount of flow had taken place within the dykes after magnetization had occurred. The opinion of petrologists seems to be that such basic material cannot be still fluid at temperatures as low as the Curie point of magnetite. This effect merits further study.

Bruckshaw and Vincenz (1954) have investigated the magnetization of the Tertiary lavas of the Isle of Mull, from which centre of igneous activity the Tholeiite dykes referred to above radiate. They found 16 reversely magnetized lavas, the mean declination being 173° and the mean inclination being −79°.

Vincenz (1954) extended the work to the intrusives of the Isle of Mull and finds in these examples of both reversely and normally magnetized bodies.

Hospers and Charlesworth (1954) have investigated the magnetization of the Lower Basalts of Northern Ireland. These lavas separated from the Upper Basalts by the so-called interbasaltic horizon were considered to be Eocene but recently Simpson has presented arguments in favour of a Miocene age. Hospers and Charlesworth sampled between 5 and 7 flows at four different localities. All the flows were found to be reversely magnetized. The mean direction for all the 24 flows is shown below.

Table 5. Magnetization of the Tertiary Lavas of N. Ireland

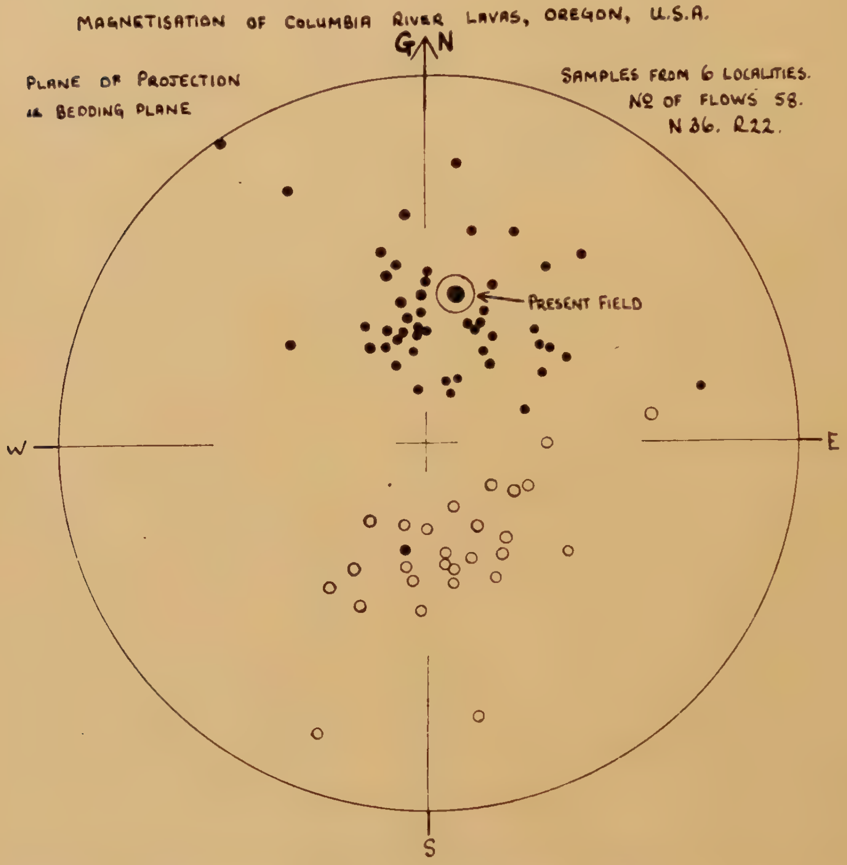
	Declination	Inclination	Angle with mean direction
Mean direction	N.194°E.	−60·2°	0°
Present field	N.13°W.	+70°	180°−15°
Dipole field	N.0°	+70·8°	180°−11·5°
Radius of circle of confidence=5·4°			

Bullerwell (1954) has also shown by magnetic survey across the edge of lava flows in Northern Ireland that some flows are reversely magnetized. He also showed the presence of normally magnetized flows which Hospers and Charlesworth did not find.

There is thus no indication that the magnetization of the Northern Ireland flows is any different from the Icelandic flows except in one particular. The mean direction of magnetization found by Hospers and Charlesworth imply a pole at 133° E. 76° N. and they interpret this as a possible movement of the pole of rotation (assuming the N. Ireland lava flows to be older than the Icelandic flows). This interpretation is of course open to question. The 24 flows sampled may have erupted within a short space of time so that the magnetizations may represent the deviation of the magnetic field due to the secular variation rather than any movement of the mean pole.

Campbell and Runcorn (1955) have shown that the Columbia River basalts of Miocene age of Oregon and Washington, U.S.A., show the same alternating zones of normal and reversed magnetization which Hospers found in Iceland. A stereogram of the preliminary results is shown in fig. 7. The mean number of flows between successive reversals is 7 compared with 20 in Iceland. It is therefore possible that the average rate of eruption of lava flows was more than twice as quick on the Columbia plateau as in Iceland. Campbell and Runcorn find 4 lava flows lying between a normally and reversely magnetized series which are magnetized in directions widely different from these predominant directions. They interpret this as evidence of a reversal of the field, for reversal due to the anomalous properties of the iron oxide minerals would not be expected to result in oblique directions of this kind. Such a search for intermediate zones at which the process of reversal is actually observed to take place seems likely to prove to be of key importance.

Fig. 7



Stereogram of magnetization of the Columbia River Basalts (Campbell's data). Notation used throughout: ○ Upper hemisphere. ● Lower hemisphere.

Roche (1950, 1951, 1953) reports work on the Tertiary lava flows of the Central Massif of France. He shows the presence of many reversely magnetized flows. Light is thrown by the field work of Roche (1953) and by Hospers (1953) on the process by which lavas become reversely magnetized. Roche finds that a number of clays and a marly limestone, baked by overlying reversely magnetized lava flows, were invariably reversely magnetized in the same direction, even when the clays were not derived from rocks of volcanic origin. Hospers found a reversely magnetized dyke, probably Quaternary, cutting a series of normally magnetized Tertiary lava flows. The contact zone in the lavas, which had at the time of intrusion of the dyke been heated above the Curie point, was magnetized in the same direction as the dyke.

No successful demonstration that the reversely and normally magnetized lavas are dissimilar in their petrological or physical properties has ever been reported, though the complexity of the iron oxide minerals and the rudimentary stage of our knowledge of them is important to recall in this connection. It is interesting to note that the intensity of magnetization (I^r) and the magnetic susceptibilities (k) are nearly the same for reversely (R) and normally (N) magnetized lavas as shown in table 6.

Table 6. Roche and Hosper's Comparison of Normally and Reversely Magnetized Lavas

		Mean I^r	Mean k
Miocene France	N	$1{\cdot}20 \times 10^{-3}$ gauss	$0{\cdot}32 \times 10^{-3}$
	R	$1{\cdot}14 \times 10^{-3}$ gauss	$0{\cdot}31 \times 10^{-3}$
Early Quaternary Iceland	N	$4{\cdot}99 \times 10^{-3}$ gauss	$1{\cdot}05 \times 10^{-3}$
	R	$4{\cdot}93 \times 10^{-3}$ gauss	$1{\cdot}11 \times 10^{-3}$
Tertiary Iceland	N	$3{\cdot}02 \times 10^{-3}$ gauss	$1{\cdot}18 \times 10^{-3}$
	R	$4{\cdot}27 \times 10^{-3}$ gauss	$1{\cdot}14 \times 10^{-3}$

It is important to estimate the length of time elapsing between geomagnetic reversals—a rough estimate suggests between a few hundred thousand and a million years on the average but of course there is no reason to suppose it is regular.

Hospers found examples of reversely magnetized sediments in Iceland which had evidently not been baked by volcanic action. A thick series of Pliocene sediments at Tjornes were found, normally magnetized at the top and reversely magnetized at the bottom.

This general picture is in contradiction to that of Torreson, Murphy and Graham (1949), who have examined the magnetization of 99 samples of flat-lying, undisturbed sediments, mainly Tertiary but including a few Jurassic. They find a very strong tendency for the directions of magnetization to be grouped along the direction of the geocentric axial dipole field, in declination markedly and in inclination moderately different from the present direction of the geomagnetic field. Though there is a tail to the distribution, eight specimens being reversed, there is no evidence of even a small peak opposite to the main one. The authors concluded that this evidence was consistent with the idea that for the past 50 million years or so the polarity of the earth's field had not changed but that its mean direction had been close to that of the field of an axial dipole. However, they were able to provide no evidence, either of a field or laboratory type, to demonstrate the stability of the sediments which they measured. Consequently their results must be discounted.

Kawai (1951) investigated the magnetization of Tertiary sediments and lava flows in Japan, see table 7. He was able to sample in the Bôsô sedimentary basin in which continuous deposition took place in a geosyncline. He finds the fluctuation in declination to lie between N. 30° E. and N. 30° W.

Table 7. Magnetization of Canaeozoic Sediments from Japan

Geological age	Declination	Inclination	No. of samples	Geological dip of strata to North
Pleistocene	N.6·2°W.	+44·8°	35	8°
Upper Pliocene	N.4·0°W.	+39·7°	31	12°
Lower Pliocene	N.3·8°W.	+24·3°	16	12°
Miocene	N.1·5°W.	+28·3°	65	±0–50°

The trend with time in declination and inclination is of interest, the large change in the latter being similar to that found in ocean cores by Johnson, Murphy and Torreson (1948). Negative inclinations of up to 10° were observed in some of the Miocene sediments. The likely explanation of this variation is that since the earth movements, which have tilted the strata to the north and have produced an anticlinal fold (roughly E.–W.) in the Miocene beds, the rocks have received a certain amount of I.R.M. Assuming the present direction of the geomagnetic field has not changed for the order of a million years and the tilting occurred about the same time, the effect should be to reduce the magnetic inclination.

The most striking feature of the results is the absence of any reversed magnetizations. In view of the fact that Kawai was not able to prove the stability of the material on which he worked and that considerable remagnetization has had to be assumed to account for the variation of inclination, we must assume that geomagnetic reversals even if they occurred would probably not be recorded in these beds.

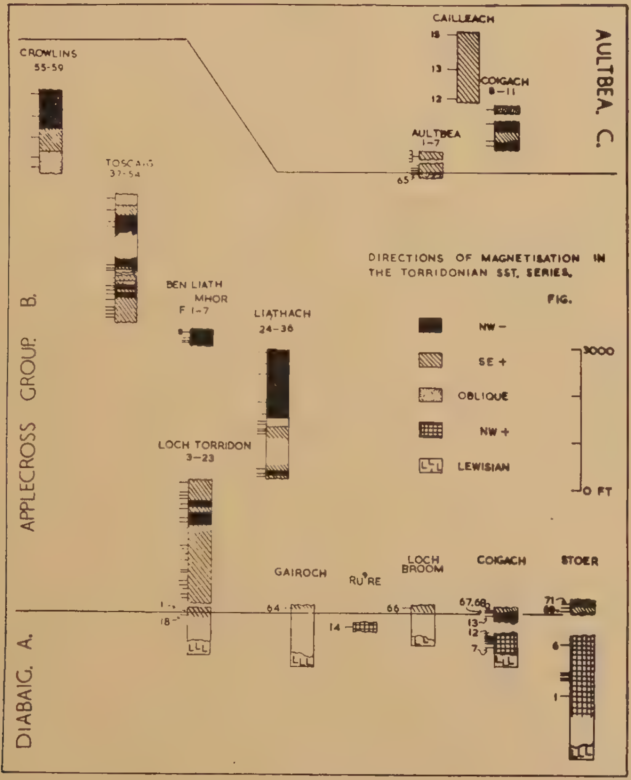
Kawai also examined the Upper Neogene (Plio–Pleistocene) sediments and volcanic rocks in Kinki district and the Mio–Pliocene rocks in Toyama district. Again the sandy and silty part of the Kinki sedimentary material, which proved to be sufficiently magnetized to be measured, was magnetized along the present direction of the geomagnetic field, except for the Azuki tuff which was reversely magnetized.

The magnetizations of 12 Setouti lava flows from the Kinki district are reversed in the case of the intermediate eruptions and are normal for the earlier and later ones. It is however of great importance that measurements in Tertiary sediments of comparable completeness to those made on the lavas should be obtained. An interesting test of the hypothesis of geomagnetic reversals will then be possible. If sufficient data are obtained randomly distributed through Tertiary times it should be found that the ratio of reversely to normally magnetized specimens should be the same for different parts of the world.

§ 11. Palaeomagnetism of the Pre-Cambrian

The first extensive survey of the magnetization of a single sedimentary formation was undertaken by the Department of Geodesy and Geophysics, Cambridge University and is reported by Irving (1954). Because of the interest of its extreme age coupled with the fact that the strata had not been seriously tilted or metamorphosed, the Torridonian sandstones of N.W. Scotland were chosen. Outcrops of these late Pre-Cambrian sandstones may be arranged in a rough stratigraphical sequence as in fig. 8. It appears that in the upper Applecross and Aultbea groups two predominant polarizations exist; a N.W. declination with a negative inclination and a S.E. declination with a positive inclination. Sandwiched between these were found, in some instances, 'oblique' zones in which the directions were widely scattered and different from the predominant

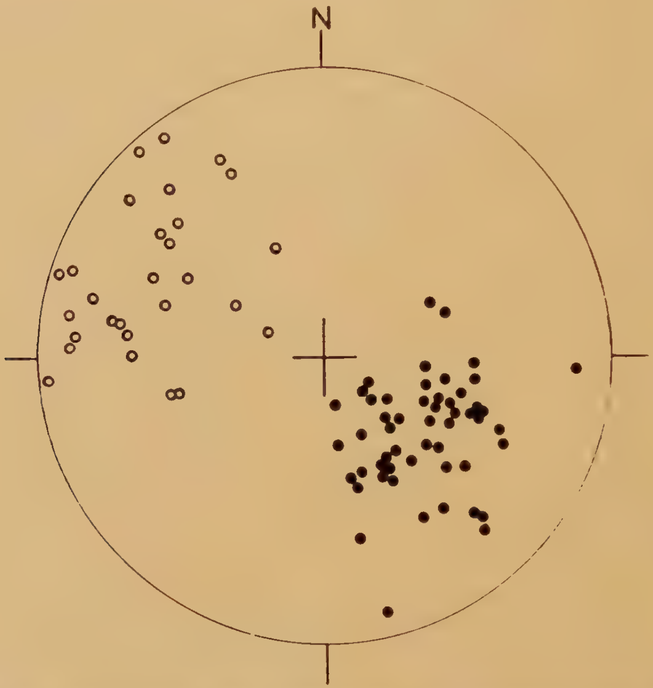
Fig. 8



Palaeomagnetic stratigraphical column for the Torridonian Sandstones of Scotland (Irving's data).

directions. Inspection shows that the N.W. and S.E. directions are nearly opposite—the reversals being similar to those of the Tertiary lava flows (see fig. 9). The usual statistical treatment shows that the two predominant mean directions are almost at 180° with each other. Creer (1955) shows the Longmyndian of Shropshire of late Pre-Cambrian age to contain red sandstones similarly magnetized to those of the Applecross and Aultbea groups of the Torridonian.

Fig. 9



Mean directions of magnetization in Torridonian Sandstones.

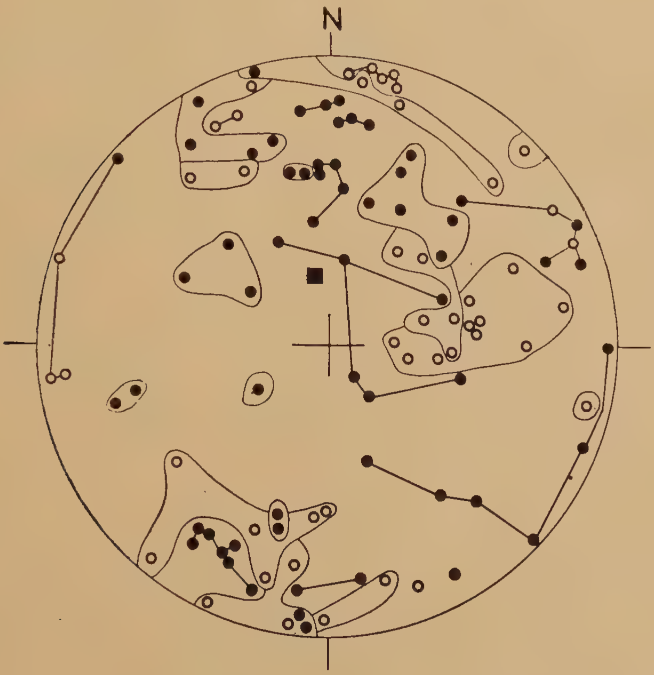
Table 8. Comparison of Directions of Magnetization in Pre-Cambrian of Gt. Britain

	Declination	Inclination	α	κ
Applecross and Aultbea	127° 295°	+52° −34°	6° 9°	14·0 11·8
Longmyndian	294°	−29°	12°	4·9
Diabaig Group	307	+34°	7°	40·0

The lower group of the Torridonian, thought by geologists to be very likely much older than the upper two groups, has been found by Irving to be magnetized in a very different direction. Table 8 shows these results.

Irving studied in detail the field evidence for the stability of these magnetizations, using the methods of Graham (1949). He studied the dispersion of the present directions of polarization of pebbles of fine and very fine Torridonian sandstones in conglomerate beds of New Red Sandstone Age. He finds $\kappa = 1{\cdot}1$ and $1{\cdot}3$ for beds of definite and presumed N.R.S. age. The results shown in fig. 10 give the directions of magnetization of samples cut from 47 conglomerate pebbles. The results for discs from the same pebble are linked together by lines in the case of presumed N.R.S. age, and are enclosed for definite N.R.S. age.

Fig. 10



Direction of magnetization of fine-grained Torridonian pebbles in N.R.S. conglomerates.

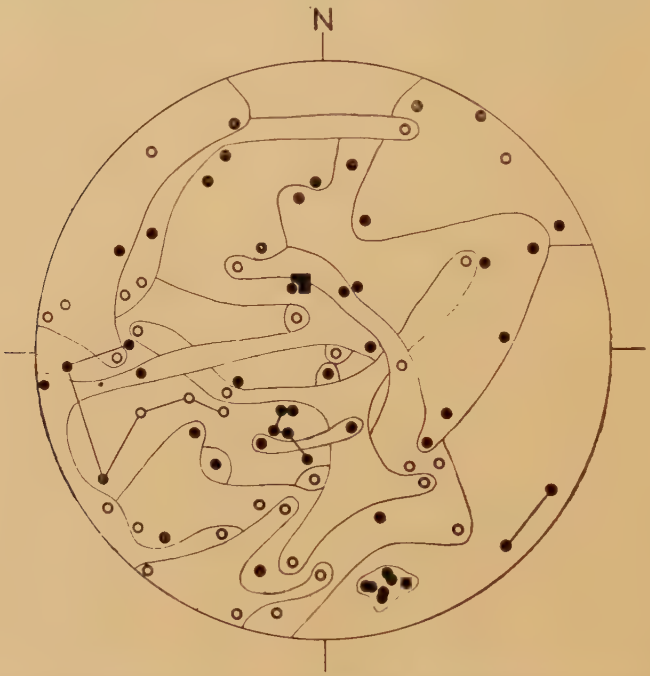
■ =direction of the present geomagnetic field.

On the other hand the polarizations of discs cut from coarse-grained pebbles in these same conglomerate beds show wide internal dispersions (see fig. 11) in very much the same way as Irving found in discs cut from coarse-grained sandstones in their original positions.

Irving (1954) has examined a steep Caledonian fold in the fine and very fine Torridonian sandstones on the S.W. slopes of Ben Lioth Mhor. Figure 12 gives the directions without corrections for geological dip and fig. 13 gives the same directions after correction. The κ for the mean directions at the eight different sites is $4{\cdot}4$ before correction and $25{\cdot}5$

after correction. This represents an extremely convincing example of the stability of sedimentary magnetization over a considerable proportion of geological time. Irving has examined the magnetization of two zones of knotted folds with amplitudes between 0·1 and 10 cm. between which lie flat bedded layers, uniformly magnetized in a N.W. direction.

Fig. 11



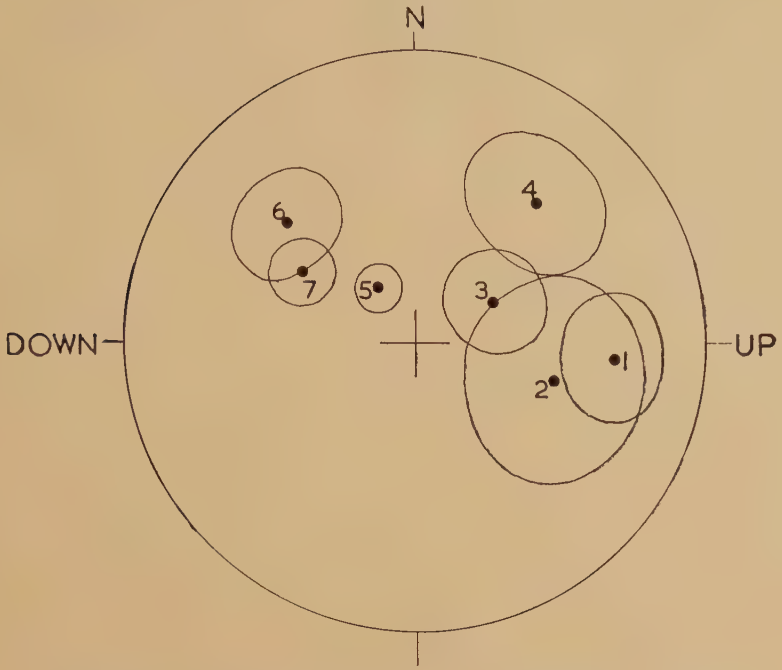
Direction of magnetization of coarse-grained Torridonian pebbles in N.R.S. conglomerates.

■ =direction of the present geomagnetic field.

Figures 14 and 15 show the present polarization of samples of these very fine sandstone slumps in which one group has clearly been magnetized after slumping and one group clearly before. Development of such studies will clearly be of great importance in determining the exact time of origin of the magnetization of rocks. It is possible, as has been noted by Clegg, that if a sediment is very full of water, change of direction of the ambient field may succeed in reorienting the magnetic grains. Consequently in some sediments the magnetization may be finally determined some little time after deposition.

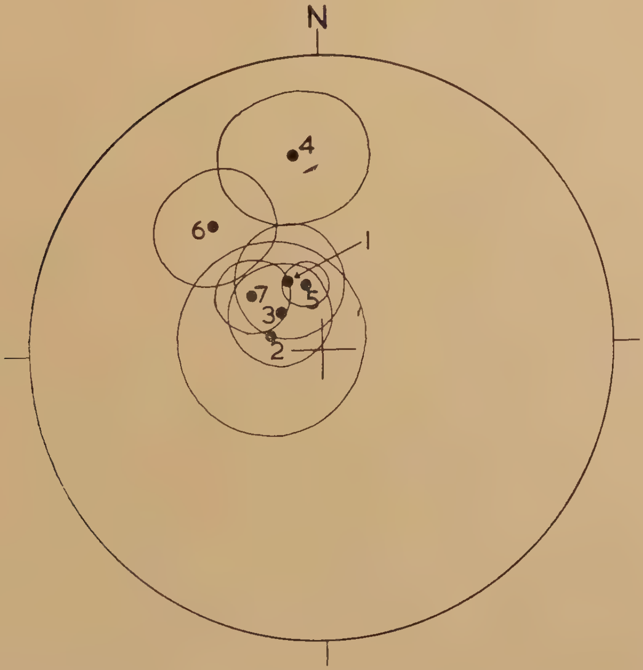
A particularly impressive proof that certain of the Torridonian Sandstones are highly stable has been found by Irving who has shown that the directions of magnetization of 10 blocks taken from an interformational conglomerate at Stoer in the Diabaig sequence are randomly orientated with $\kappa=1{\cdot}6$. Figure 16 shows a stereogram of the results.

Fig. 12



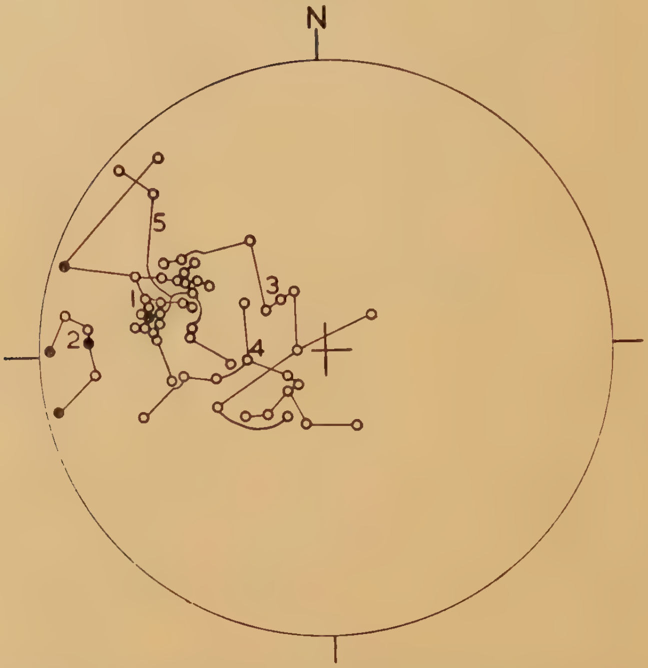
Direction of magnetization of Caledonian fold before correction for geological dip (Irving's data).

Fig. 13



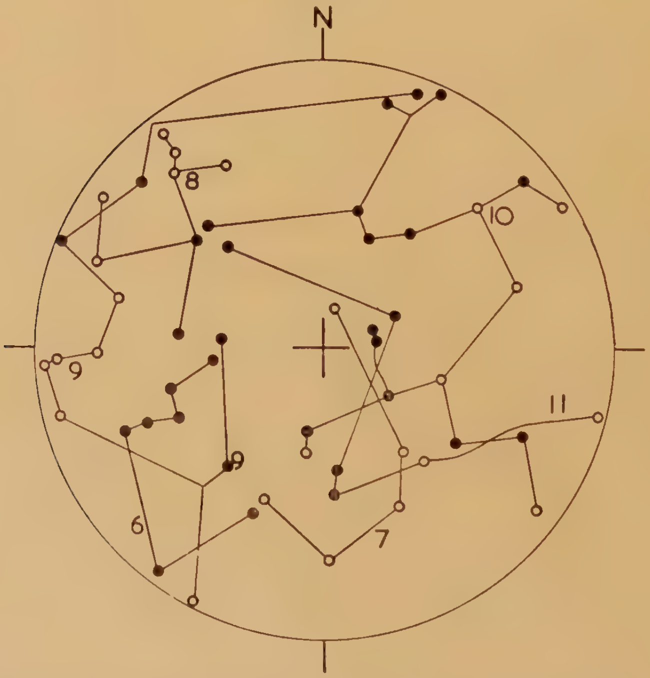
Direction of magnetization of Caledonian fold after correction for geological dip (Irving's data).

Fig. 14



Direction of magnetization in slumped beds (Irving's data).

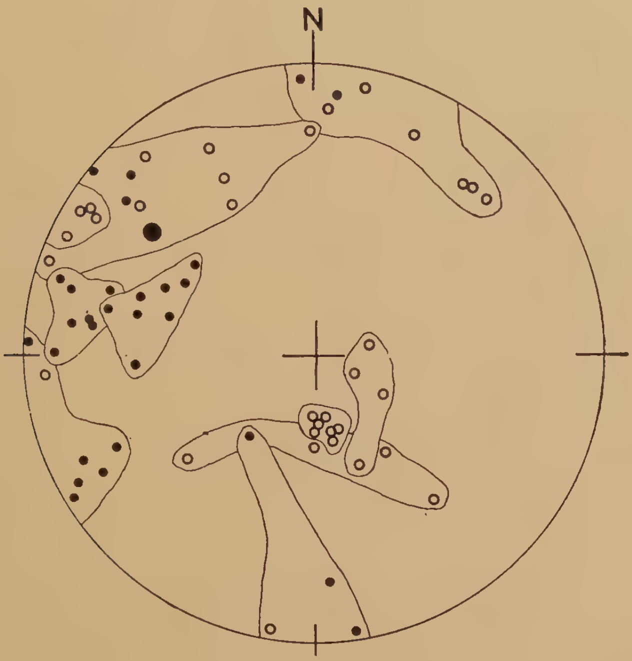
Fig. 15



Direction of magnetization in slumped beds (Irving's data).

Du Bois (1955) has determined the directions of magnetization for specimens of the Middle and Upper Keweenawan of N. Michigan. The Freda sandstone and Nonesuch Shales of the Upper Keweenawan have a mean declination of 75° west of north and a mean inclination of 0°. From sandstones in the underlying Copper Habor Conglomerate of the Upper Keweenawan and the Portage Lake Lava series of the Middle Keweenawan a mean declination of 70° West of North and a mean positive inclination of 40° has been obtained.

Fig. 16



Direction of magnetization of blocks from interformational conglomerates at Stoer.

● =direction of magnetization of enclosing, well-bedded layers.

Graham (1953) has determined the direction of magnetization of a group of Pre-Cambrian diabase dykes of Michigan. Some of the dykes show a very scattered magnetization, which he attributes to chemical changes. The magnetization of the Covington 1·8 ft. dyke and the Taylor Mine 40 ft. dyke are consistently magnetized with a mean declination of 270° and an inclination of −85°.

§ 12. Palaeomagnetism of the Mesozoic (70–190 million years)

Clegg, Almond and Stubbs (1954) have measured the natural remanent magnetization of Triassic sediments in England, in nine sites over a wide area. They find the Keuper Marls to be magnetized in a North East–South West direction. The mean values as recalculated by Creer (1955) are shown in table 9.

Table 9. Direction of Magnetization of the Triassic Sandstones of England

Declination	Inclination	α	κ
N. 29° E.	$+34°$	10°	58
S. 39° W.	$-16°$	27°	13

§13. PALAEOMAGNETIZATION OF THE PALAEOZOIC (190–500 million years)

Important surveys of the magnetizations of Palaeozoic rocks have been made by Graham (1954 a), by Creer (1955) and by Gough (1955).

Graham reports measurements on 182 samples from the Eastern United States of Ordovician to Permian age. The polarizations are somewhat scattered but are grouped about the present direction of the geomagnetic field. Graham concluded tentatively that because the beds sampled are flat lying and undisturbed, the results could be taken as implying that for most of Palaeozoic time the direction and sense of the geomagnetic field were very much as they are today. In the absence of any tests for stability these results must probably be discounted.

Creer selected from Palaeozoic rocks in Britain those fine-grained red sandstones and siltstones which experience with the Torridonian strata had shown to be likely to be magnetically stable. Creer sampled a stratigraphical thickness of 350 ft. of purple Caerbwdy sandstones at Caerbwdy Bay, S. Wales. He showed that the correction for the dip of the beds, about 50° towards the south, decreased the scatter of the magnetizations, thereby suggesting that they were stable. This he also confirmed by re-measuring the specimens after some months in the laboratory. Creer obtained a mean declination of S. 7° W. and a mean inclination of $+39°$, with a value of α of 8° and a value of κ of 32·4.

Creer also sampled extensively the Old Red Sandstone rocks of the Anglo-Welsh Cuvette. His results are summarized in table 10. Unlike the Pre-Cambrian and Mesozoic results referred to above it is surprising that Creer finds no reversals of magnetization in any lower Palaeozoic rocks. If further search in Palaeozoic rocks in Great Britain reveals very few reversals then this will open the way to a decisive test of the hypothesis of field reversals, as a similar situation should be found in other parts of the world.

Recently D. I. Gough of the National Physical Laboratory, South African Council for Scientific and Industrial Research, has made a thorough study of the directions of magnetization of the Pilansberg dykes near Johannesburg, the reversed magnetization of which has long been known from magnetic surveys. Two hundred specimens from outcrops of these dykes were measured and found to show random directions of magnetization and variations in intensity between 1×10^{-3} and 570×10^{-3} gauss. Magnetization by lightning or during weathering was suspected and so five of the dykes were sampled at depth in the gold mines of the Witwatersrand. The East Geduld dyke shows 4 specimens magnetized opposite to the other 58 specimens. Three of these have a very low intensity of magnetization and therefore may have acquired sufficient I.R.M. in the present field to obscure their reversed magnetization. The Goch dyke is composite and the inner part (see fig. 20) is much more weakly magnetized than the outer part and has a low inclination, which may possibly be due to isothermal remanent magnetization in the present geomagnetic field.

Table 10. Mean Directions from 15 Sites in the Old Red Sandstone (Creer's data)

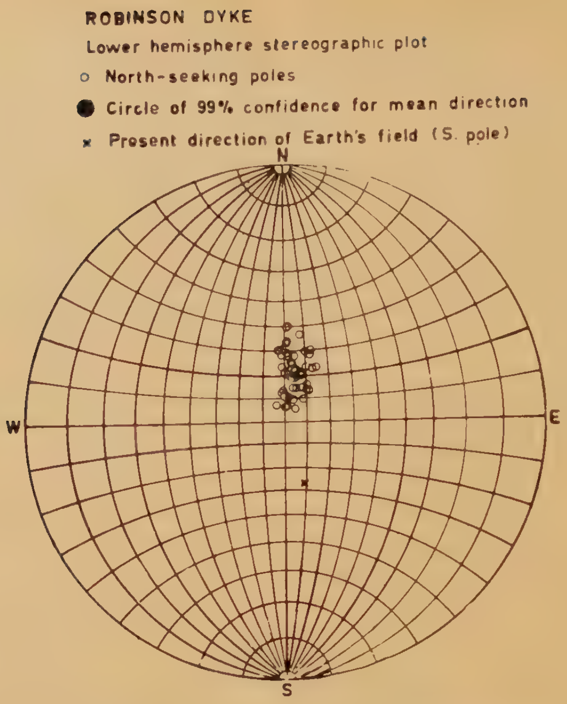
D	*I*	α	κ	Direction of geological tilt of beds
S.20° W.	+ 6	12°	36	Flat lying
S.14° W.	−12	5°	115	
S.14° W.	− 8	9°	60	
S.15° W.	+ 2	10°	37	
S.16° W.	−10	15°	37	
S.28° W.	+10	8°	27	
S.22° W.	+25	11°	7	
S.19° W.	+21	6°	57	E. Moderate
S.16° W.	−16	7°	61	SE.
S.19° W.	+21	6°	57	N. Almost vertical
S.32° W.	+31	17°	28	N.
S.55° W.	+36	23°	17	N.
S.29° W.	−33	14°	23	S.
S.25° W.	−36	14°	33	S.
S.42° W.	−25	29°	19	S.

Table 11

Dyke	No. of samples	Declin-ation	Inclin-ation	Range of Intensities	Circle of con-fidence	
Robinson	45	11·4°	68·1°	$0{\cdot}86\times10^{-3}$—$6{\cdot}1\times10^{-3}$	2·4°	see fig. 17
E. Geduld	58	31·1°	69·6°	$0{\cdot}039\times10^{-3}$—$14{\cdot}0\times10^{-3}$	2·8°	see fig. 18
Goch		9·4°	58·8°		3·6°	see fig. 19

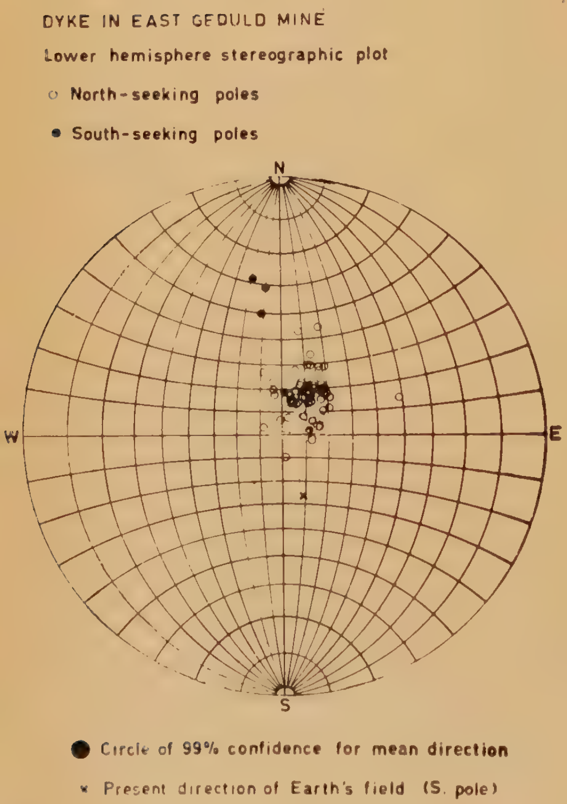
The Pilansberg dykes are post Waterberg and pre-Karroo according to du Toit (1954) and Cooke (1953) dates the Waterberg at 400 million years and the Karroo at 300 million years. However, their age is in doubt and they may be late Pre-Cambrian.

Fig. 17



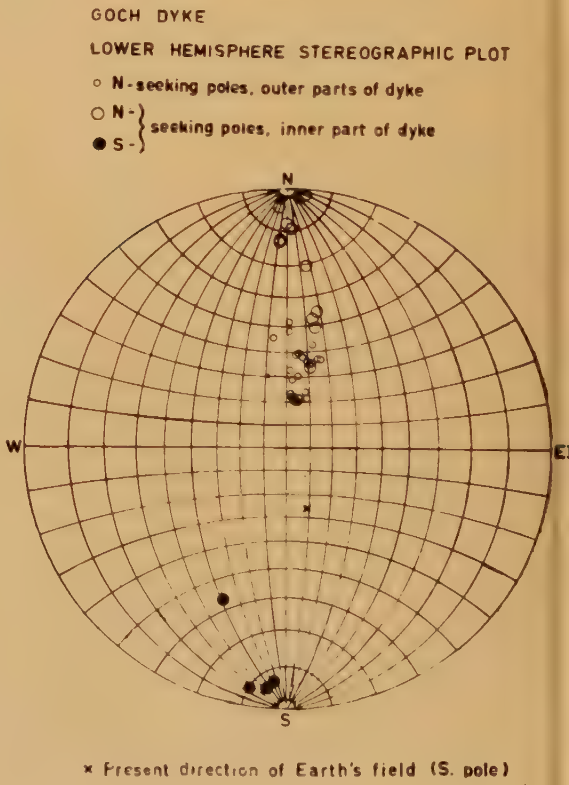
Direction of magnetization. Robinson Dyke Pilansberg system (Gough's data).

Fig. 18



Direction of magnetization. East Geduld Mine
Pilansberg system (Gough's data).

Fig. 19

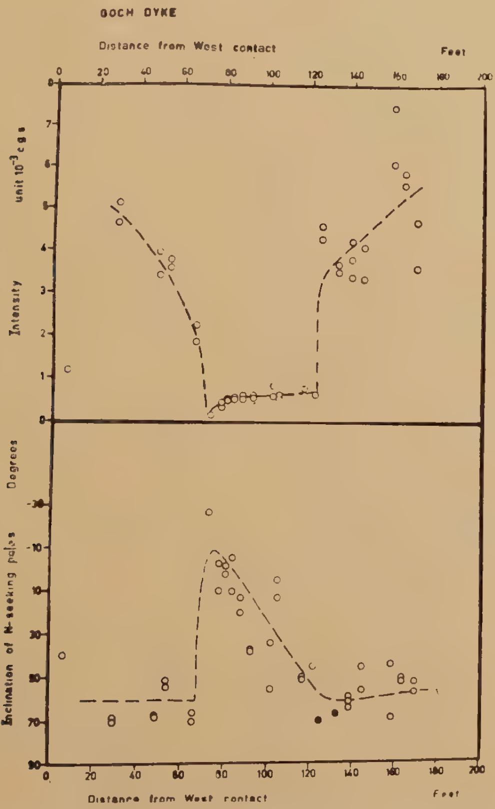


Direction of Magnetization. Goch Mine
Pilansberg system (Gough's data).

Hallimond and Butler (1949) had long ago concluded that the Whin Sill of N. England, which was intruded in Carboniferous times, was horizontally magnetized and reversed with respect to the horizontal component of the present field.

J. C. Belshé (1955) has measured samples of the Lower Carboniferous of Derbyshire and finds a mean declination of N. 26° E. and a mean positive inclination of 43° for the toadstones and 37° for the sandstones and siltstones. Belshé also finds horizontal magnetizations in igneous rocks from Queen Maud's Land in Antarctica. These have an uncertain late Palaeozoic age.

Fig. 20



Intensity and inclination across Goch Mine Pilansberg system (Gough's data).

Distance from West contact in feet. Inclination of N.-seeking poles in degrees. Intensity unit 10^{-3} c.g.s.

Creer (1954) also sampled five traps of the Permian lavas of Devon giving a mean declination of S. 9° W. and an inclination of −9°. The radius of confidence at the 5° level was 20° and the value of $\kappa = 15$.

It is of considerable interest that Mercanton (1926) found from a number of specimens that a Permian lava between Keania and Wollogong in New South Wales was reversely magnetized with an angle of inclination of −87°.

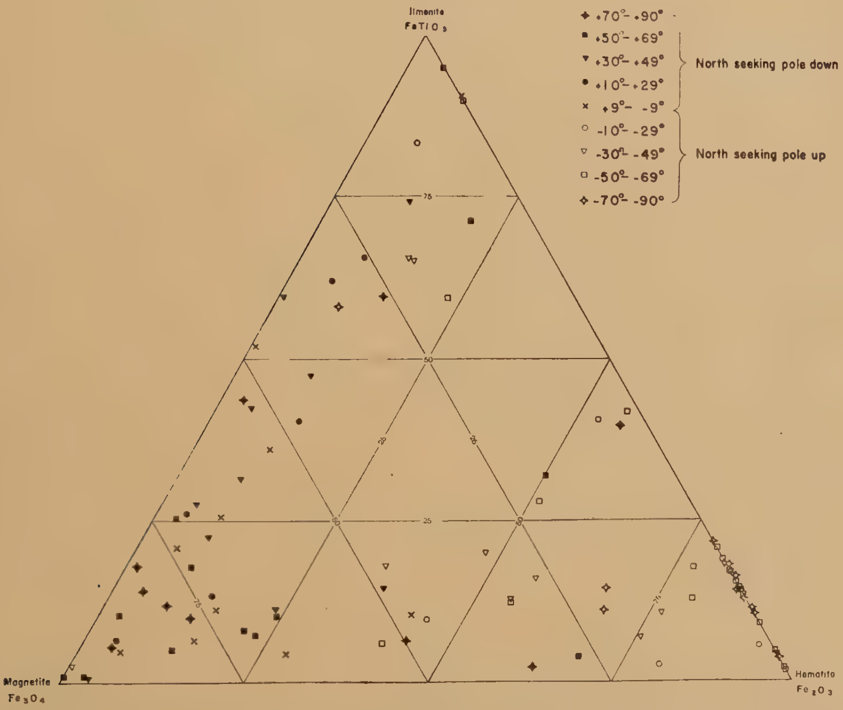
It may thus be noted that Palaeozoic lavas and sediments are magnetized at angles appropriate to latitudes 60°–90° from those of their present location.

§ 14. THE ORIGIN OF REVERSED MAGNETIZATION

It is now clear that reversals of magnetization commonly occur in quite small thicknesses in much of the geological column, all over the world and in both sediments and igneous rocks. When Heiland (1930) discussed the origin of reversed magnetization, the examples were so few and scattered that local causes such as lightning and mechanical stresses seemed plausible. And in fact Pockels had demonstrated the remarkable, though small scale, anomalies which are caused in igneous rocks struck by lightning. The reversed magnetization of the Pilarsberg dykes in South Africa and the Tholeiite dykes of N. England, with the later discoveries in the plateau basalts excluded such local causes and made it necessary to infer either reversals of the geomagnetic field or a property of spontaneous reversal of magnetization in the minerals.

The possible correlation of reversed magnetization with the presence in the rocks of certain minerals arises most directly in the work of Balsley and Buddington (1955). They are concerned with the explanation of large magnetic anomalies in the Adirondack Mountains, New York, revealed by aeromagnetic survey. Two hundred specimens of varied igneous and metamorphic rocks were collected. Buddington and Balsley find that the rocks showing normal magnetization in the field contain as accessory minerals magnetite with exsolved intergrowths of ilmenite and ulvöspinel—the Koenigsberger ratio (K) being not greater than 1. In rocks showing reversed magnetization they find the accessory minerals are exclusively members of the haematite–ilmenite rutile series. Rocks in this group have a large Koenigsberger ratio and coercive force (the titanohaematites have $K=1700$ and a coercive force of more than 2000 gauss). Buddington and Balsley find also a third group of rocks in which both the magnetite ilmenite and the haematite ilmenite rutile series occur. This group has directions of magnetization transitional between those of the other two groups (reversed and normal)—only the values of magnetic inclination and total intensity are given by Buddington and Balsley. These results are shown in figs. 21, 22 and 23. Buddington and Balsley conclude that the strong magnetization of the reversed group must have been acquired by the haematite–ilmenite–rutile series in the presence of a field not dissimilar to that existing at the present day. The writer disagrees with this interpretation on a number of grounds. Firstly the magnetization found in the Adirondack rocks is reversed only in the sense that N. poles appear on the top surface of the rocks. In fact we infer that the reversed directions of magnetization make an angle of 140° rather than 180° with the present geomagnetic field. If it is assumed that the magnetite–ilmenite group is magnetized along the direction of the present geomagnetic field, whether it is present in the rock alone or in varying proportions with the haematite group, then for the transitional magnetization to be understood it is necessary for the haematite to be magnetized in a direction making an obtuse angle with the present field.

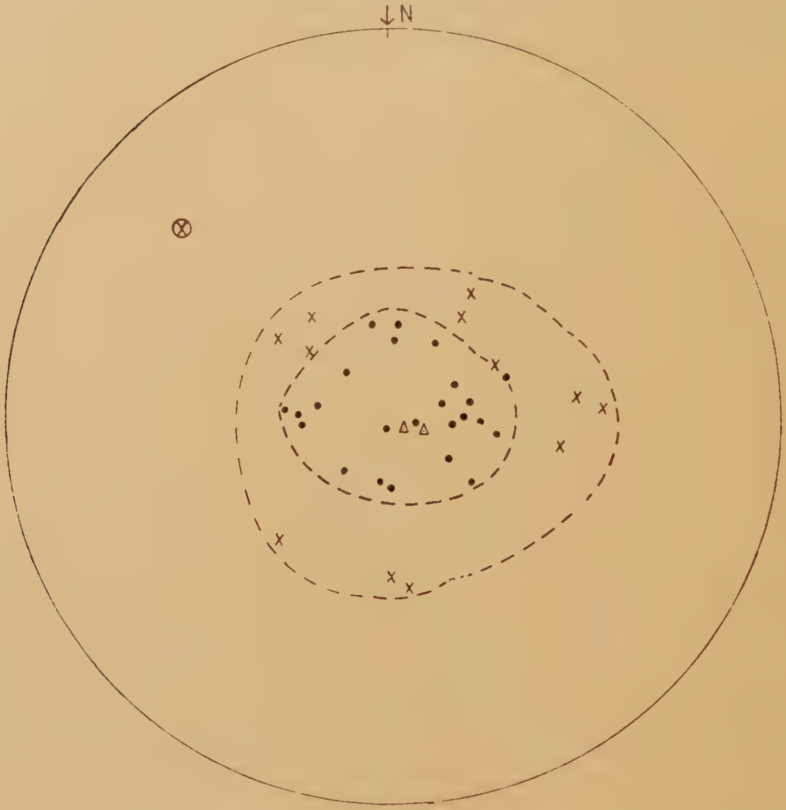
Fig. 21



Variation of magnetic properties with variation of composition of iron–titanium oxides in Adirondack rocks (Buddington's and Balsley's data).

From fig. 22, for instance, we would assume that if the magnetite is always magnetized along the present direction of the geomagnetic field then the haematite is almost vertically magnetized. Thus where both magnetite and haematite are present in one rock the direction of magnetization will be intermediate as Buddington and Balsley find. Runcorn (1954 a) suggested that the dissimilar magnetization of the magnetite and haematite might either be due to the contrasting stabilities of these two magnetic oxides suggested by their different coercive forces or that the magnetization might have been acquired at totally different times due to the dissimilar Curie points. The former hypothesis would seem the more attractive, because the process of magnetization of the haematite would in view of the high Koenigsberger ratio seem a vastly more efficient one. It is thus probably thermoremanent in origin. The low Koenigsberger ratio of the magnetite would

Fig. 22

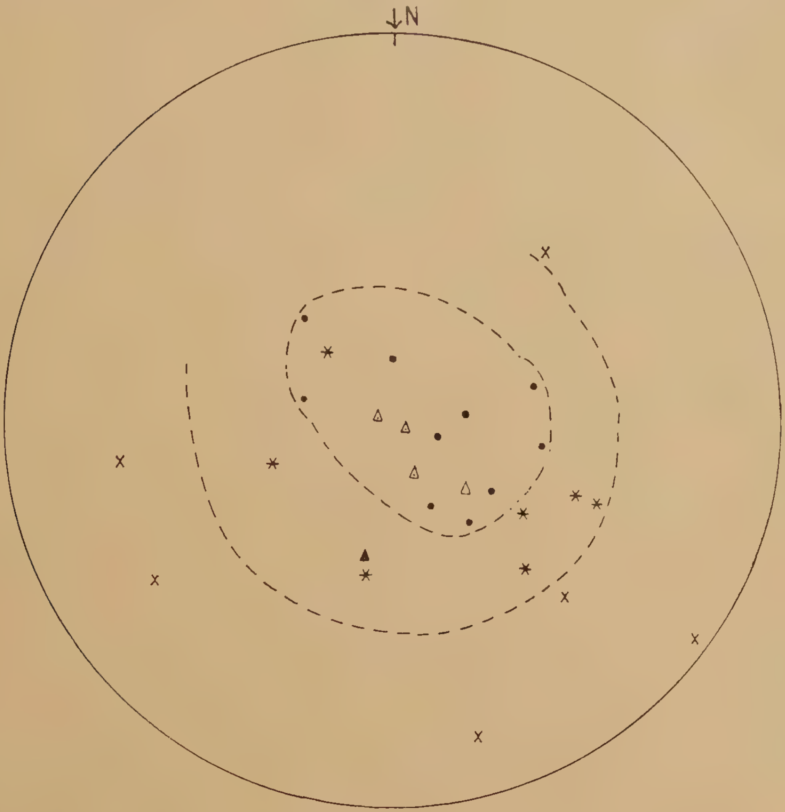


Stereogram for 39 rocks with accessory oxides consisting of magnetite (with a very little exsolved ilmenite) and ilmenohematite (titanhematite with exsolved ferricilmenite intergrowth, with or without a very little exsolved rutile intergrowth). Rocks are almost exclusively sillimanitic quartz-microcline gneiss, a product of partial granitization of biotite quartz-plagioclase gneiss. Plotted for lower hemisphere.

No. of Specimens	Symbol	Ilmenohematite as per cent of total Fe–Ti oxides	Fe_3O_4 as per cent of total Fe–Ti oxides	Inclination
24	●	100–90	0–10	−55° to −85°
12	×	90–30	10–70	−30° to −60°
2	△	30–0	70–100	+60° to +88°
1	⊕	55	45	−22°

seem to be indicative of a less effective process of magnetization even perhaps I.R.M. produced in the last few hundred thousand years. There are not sufficient results yet on this interesting problem to support this

Fig. 23



Stereogram for 28 rocks with accessory oxides consisting of magnetite (with or without exsolved ilmenite intergrowth) and ferricilmenite (ilmenite with 6–13 per cent Fe_2O_3 in solid solution) plus a very little rutile. The rocks are hornblende granite and equivalent gneiss except for 2 diorite and gabbroic anorthosite gneisses.

No. of Specimens	Symbol	Ferricilmenite as per cent of total Fe–Ti oxides	Fe_3O_4 as per cent of total Fe–Ti oxides	Inclination
10	●	100–80	0–20	−48° to −77°
6	×	70–50	30–50	+0° to +30°
7	⊛	50–25	50–75	+30° to +60°
4	△	25–0	75–100	+60° to +86°
1	▲	0	100	−50°

contention. However the present author doubts if the supposed correlation of reversed magnetization and haematite really casts doubt on the general validity of interpreting the direction of magnetization of rocks as that of an original field particularly as metamorphic rocks are, as was explained above, a special case. Nevertheless Néel has shown and reviews in his article in this volume that there are several possibilities by which an igneous rock in the course of cooling and any rock by changes of chemical composition or structure in its iron oxide minerals may acquire a magnetization in a direction opposite to the field at the time of original magnetization. Nagata (1953) has discovered in the Haruna dacite the actual occurrence of such a Néel reversal. It remains to discuss whether such a process may account for an appreciable fraction of the reversals found in nature. The difficulty in deciding this arises because in the laboratory reproduction of the process of magnetization (reheating and cooling an igneous rock or even redispersing a sediment) the anomalous property of the oxide minerals may be destroyed. Parry (private communication) has shown that even in a neutral atmosphere heating the Iceland basalts in some (though not a majority) of cases destroys the component of Curie point around 300°c and generates material of Curie point about 600°c. Though we note that extensive reheating tests have been carried out on the reversed and normal Tertiary basalts (Bruckshaw and Vincenz 1954, Vincenz 1954, Hospers 1953, 1954) we cannot regard their failure to find a Néel mechanism present as conclusive evidence that such a mechanism did not operate during the initial cooling. However, until evidence for the self-reversing mechanism can be proved in these rocks, it is legitimate to accept the measurements at their face value, as supporting evidence for geomagnetic reversals.

The widespread discovery of reversals of magnetizations in sediments (Clegg, Almond and Stubbs 1953, Irving 1954) to some extent has caused a general acceptance of the hypothesis of reversals of the geomagnetic field. It is however possible either that separate mechanisms account for the reversals in sediments and lava flows or that reversals mainly occur spontaneously long after the rock has been formed due to chemical or structural changes in the iron oxide minerals. These possibilities are not easily tested in a decisive manner. The former seems improbable where reversals occur in strata which have been studied in detail, e.g. the Torridonian and Triassic sediments in Great Britain and the Tertiary lava flows of Iceland and Oregon. In these magnetizations of opposed sign seem to occur with roughly the same frequency. It would be strange if two distinct mechanisms of reversal were equally probable in nature. The possibility that reversals occur long after the formation of the rocks is again difficult to exclude. However the lava flows contain the magnetite series as the ferromagnetic constituent, and the red sandstones, which so far have provided most of the data on sedimentary magnetism, have the haematite series as their ferromagnetic constituent. Thus a general property of self-reversal must be applicable to a wide range of the iron oxide minerals.

Definite tests between the two hypotheses are needed. If, by and large, observed reversals are due to a reversal of the geomagnetic field, one would expect the following :

(1) In the interval between opposed directions of magnetization there should be in some instances zones of transitional directions of magnetization. Such transitional zones could hardly arise from a Néel mechanism.

(2) Over the whole of geological time during which it is apparent that hundreds of reversals have occurred, the geomagnetic field should not be biased towards one polarity relative to the axis of rotation.

(3) During times in which the polarity remains constant over a sufficient time to establish geologically the contemporaneity of different strata concordant directions of magnetization should be found in strata of the same age. Apparently the results from Palaeozoic rocks in Great Britain indicate that this test may be feasible.

(4) No systematic differences in the physical or chemical properties of the iron oxide minerals in oppositely magnetized rocks should be found.

The hypothesis that self reversal of magnetization is a common explanation of reversely magnetized rocks seems to the writer to be defective as a hypothesis in that the conditions under which it occurs have not been yet formulated quantitatively or in a way by which tests can be applied (see Runcorn 1954 b).

§ 15. THEORETICAL INTERPRETATION OF REVERSALS

The present state of theories of the main geomagnetic field allows neither a full understanding of its polarity nor of its axial character. The demonstration (Runcorn, Benson, Moore and Griffiths 1951, Blackett 1952) that the field has no ‘ fundamental ’ significance as an example of a widely based law of physics removes any obvious connection between the polarity of the field and the sense of rotation of the earth. Consideration of the rapid secular variation of the geomagnetic elements at those places on the earth's surface where observatories have existed in the last few centuries makes it plausible that the origin of the field lies in the motions of the liquid, metallic core, the radius of which is 0·55 of that of the earth. The longest free decay time of electric currents flowing in the core is about 10 000 years so that electromotive forces must be assumed to exist. Elsasser (1946, 1947) and Bullard (1954) consider these to be entirely Lorentz forces due to the core motions—the energy being derived ultimately from the generation of heat which causes the thermal instability. Such a dynamo theory could explain reversals in two ways. The regeneration of the field could stop and the field decay. A new field in a different direction could then be built up for the sense of the final field not only depends on the velocity field but on the sign of the small adventitious field which provides the starting point of the process. The reason for this is that the dynamo theory is concerned with the solutions of Maxwell's equation with a motional induction term which reduces to the following :

$$\text{curl}^2\,\mathbf{H}=4\pi\sigma\,\text{curl}\,\mathbf{v}\wedge\mathbf{H} \quad . \; . \; . \; . \; . \; . \; . \quad (5)$$

where σ is the electrical conductivity, $\mathbf{v}$ the velocity field and $\mathbf{H}$ the magnetic field may clearly have either sign for any $\mathbf{v}$ field.

It is probable however that within the earth there are in addition to the dipole field electric mode magnetic fields which have magnitudes estimated at some hundreds of gauss. Though these do not have a radial component and therefore their existence has to be inferred in various ways they feature prominently in both the dynamo theory of the field (Elsasser 1947) and Bullard (1954) and in the thermoelectric theory of the field (Runcorn 1954 a). In both cases the dipole field results from an interaction of convective motions within the core with such electric mode fields. It seems that the polarity of the resulting dipole field depends critically on the exact form of the radial variation of the velocity field (Bullard 1954, Runcorn 1955).

Thus we can envisage the process of field reversals on the Bullard–Elsasser theory in two ways. On the one hand a change in the motions in the core may cause the regeneration of the field to cease. It then decays away in some thousands of years. The dynamo starts up again possibly using a remnant of the former field as the starting point, which may or may not lead to a dipole in the same sense as before. During the decay the surface field would be expected to be much reduced and not necessarily dipolar in character. Alternatively it is possible that the sign of the field could be reversed by a change in the fluid motion pattern without the fields within the earth decreasing. In this case the reversal might be accompanied by strong non-dipole fields at the earth's surface.

In a general approach Runcorn (1955) suggests that the electric mode magnetic fields, arising perhaps from a thermoelectric effect, stay substantially constant throughout geological time. The external dipole field, resulting from convection, may be reversed by changes in the latter, such as an alternation in the number of layers of convection cells. Though little study has been made as yet of the intensity of the field in remote epochs, there is some reason for believing it not to have altered greatly and this must be regarded as providing some support to the latter opinion. Thus there seems no reason why the polarity of the geomagnetic field should be of one sign rather than the other and we venture to predict that eventually it will be shown over the whole of geological time to have taken either sign for equal times. However, its axial character has a fundamental significance. Runcorn (1954) shows clearly that the Coriolis forces are predominant in the motions of the core. Though doubt exists concerning the mechanism by which the motions generate the field, this effect of the earth's rotation is so great that a large effect on the field must be assumed and symmetry considerations lead to the expectation that it will, over periods long compared to the decay time, result in an exactly axial field.

§ 16. INTERPRETATION OF THE CHANGES IN THE DIRECTION OF MAGNETIZATION THROUGH THE GEOLOGICAL COLUMN

We have seen that in many instances geological strata are found to have a characteristic mean direction of magnetization which is identified with the direction of the geomagnetic field in that particular epoch. The identification, though it must at present be tentative, is worth exploring. If the coincidence of the magnetic axis with the axis of the earth's rotation is taken as a fundamental hypothesis, the poles of the earth cannot have been in the same relative position with respect to the land masses as at present. If there has been no relative movement between the land masses then there must have been movement of the whole crust at least and more plausibly the whole earth relative to the axis of rotation in space. This is known as the hypothesis of polar wandering. Alternatively relative movement between the continents, with polar wandering as well, might be assumed. This is the theory of continental drift. Both are of interest in connection with the speculations of geologists concerning palaeoclimates and the world-wide distribution of related organisms.

Creer, Irving and Runcorn (1955) find it convenient to display the palaeomagnetic results obtained in Great Britain in terms of the polar wandering hypothesis. Table 12 and fig. 24 show their suggested positions of the N. pole at various geological epochs, corresponding to the mean directions of magnetization of the strata which have been fully described above. The evidence from other continents is as yet fragmentary. Yet it will be seen from the above discussion that all measurements of Pre-Tertiary rocks, for which reasonable evidence for stability can be given, show directions of magnetization very different from that of the geomagnetic field today in the part of the world from which the rocks were obtained. Further these directions are roughly consistent with the pole positions given for the appropriate geological epoch in table 12.

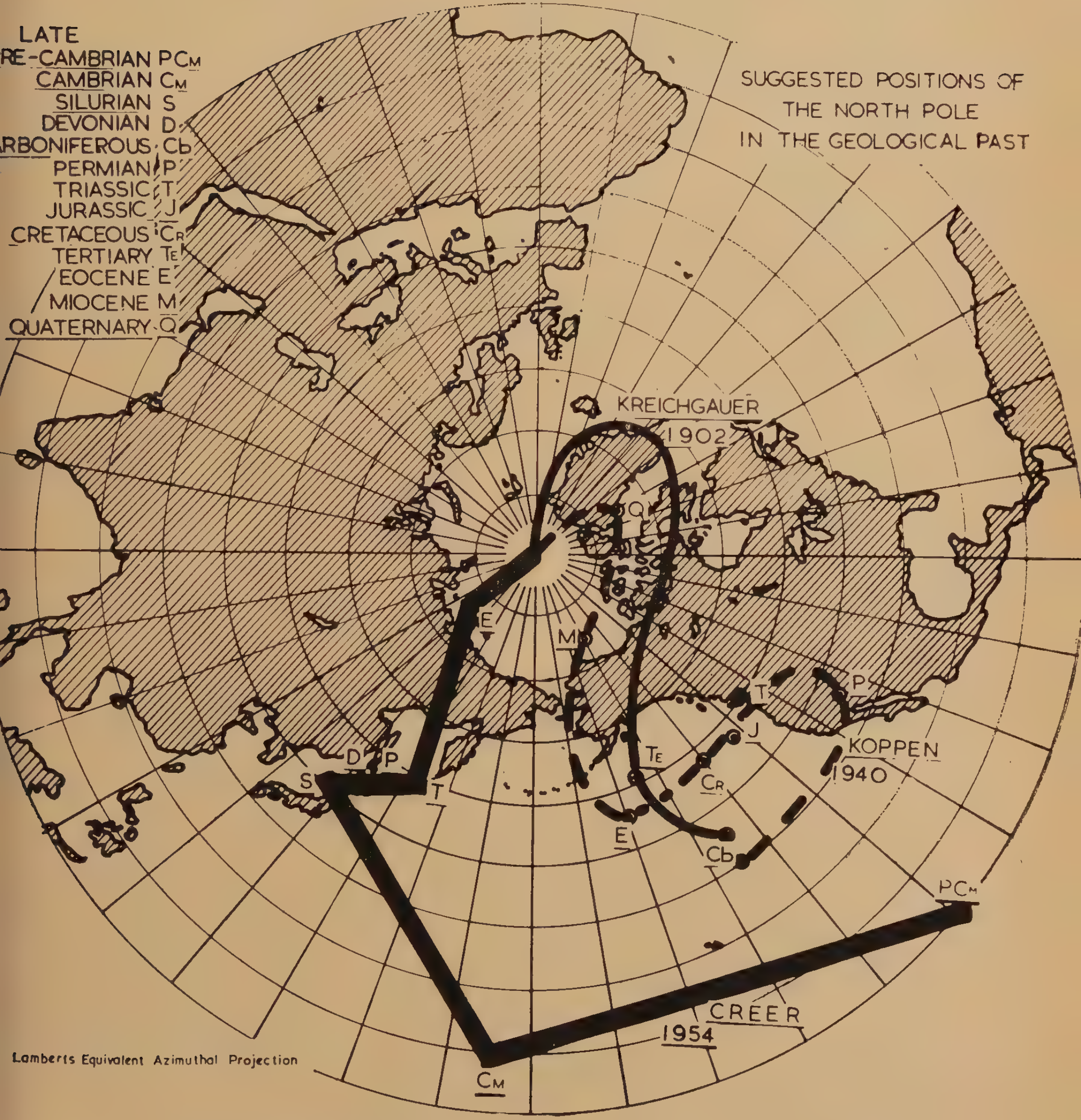
§ 17. THE HYPOTHESIS OF CONTINENTAL DRIFT

Wegener (1915) suggested that at the beginning of Carboniferous times N. America was joined to Eurasia while Africa, Australia, India and S. America formed a single continent, Gondwanaland. This hypothesis, especially in its modifications, due to du Toit, has because of its bold sweep attracted much attention. The intention of its supporters is to provide an explanation for the rapid migration of organisms throughout the world which is a feature of every stage of biological evolution. It is not clear how types with a continental habitat accomplish this and it was early postulated that extensive and transitory land bridges existed in every epoch. The theory of isostasy made it clear that the disappearance of land bridges into what is now deep ocean was unlikely, though this would not now be regarded as a valid objection. The forces which Wegener postulated as a cause of continental drift are now known to have negligible effects. Nevertheless the concept

Table 12

Geological period	Averaged directions	Polarity	Position of magnetic poles
Pre-Cambrian (Longmyndian)	N. 56 W.−38 S. 69 E.+19	N R	N. Pole—Middle of Pacific 130° W. 0° S. Pole—Near Ethiopia 50° E. 0°
Cambrian	S. 11 W.+41	R	N. Pole—Marshall Is. in Pacific 170° E. 15° N. S. Pole—Middle of S. Atlantic 10° W. 15° S.
Silurian	S. 25 W.−16	R	N. Pole—140° E. 40° N. Japan, N. Honshu S. Pole—40° W. 40° S. in S. Atlantic
Devonian	S. 18 W.−2	R	N. Pole—In Pacific nr. Kamchatka 155° E. 45° N. S. Pole—S. Atlantic about 3000 miles S.E. of Buenos Aires 25° W. 45° S.
Permian	S. 19 W.−9	R	N. Pole—In Pacific nr. Kamchatka S. Pole—3000 miles S.E. of Buenos Aires
Triassic	N. 26 E.+28	N	N. Pole—In Pacific nr. Kamchatka 155° E. 48° N.
	S. 34 W.−28	R	S. Pole—In S. Atlantic 25° W. 48° S.
Eocene	S. 14 W.−60 (Hospers, N. Ireland Lavas)	R	N. Pole—In Arctic nr. New Siberian Is. 133° E. 76° N. S. Pole—47° W. 76° S. in Weddell Sea, Antarctica

Fig. 24



Inferred positions of the pole through geological times (after Creer).

of the continents as a granitic scum (Wegener's sial) floating in a denser basaltic medium which also forms the floor of the oceans has had a powerful effect in suggesting such drift might be feasible. Jeffreys (1952) points out that however plastic the basaltic material below the continents may be because of the moderately higher temperatures, the basaltic shell under the oceans must have greater strength than the continental blocks. Drift of the continental masses through the floor of the oceans is therefore unimpressive as a geophysical hypothesis.

Jeffreys (1952) also points out that the similarity of shape of the west coast of Africa and the east coast of S. America, which figures prominently in popular expositions of continental drift is a poor fit, even allowing that the continental shelf rather than the coast is the most permanent boundary of the continental masses. It has been held that the palaeoclimates, inferred from evidence of former glaciations and from palaeontological evidence of the flourishing of plants in regions of the world which are now climatically unsuitable for them, provides strong evidence for continental drift. The meteorology of remote geological epochs is not a subject on which it would be profitable to dogmatize. Yet the widespread glaciations of South Africa, India, Australia and South America in Permian and Carboniferous times when Laurasia enjoyed mild or tropical climates requires explanation. The Dwyka tillite, or boulder clay, of South Africa can be traced from the Transvaal to the Cape and from South West Africa to Natal, in many places resting on a glaciated floor. In some cases successive glaciations, such as occurred in the Pleistocene ice age in Europe, may be recognized and it is possible to infer that the ice sheets moved towards the south.

No known mountain ranges existed to supply glaciers and it is therefore thought that the glaciation was the result of great continental ice sheets. If so the pole must have wandered far from its present position. In India similar evidence of glaciation moving northwards is found in Orissa, the Central Provinces and the Punjab.

It is often said that because this Permo-Carboniferous glaciation is contemporaneous in these four widely separated continents of the southern hemisphere, polar wandering cannot alone be the explanation. This objection is based on the same misunderstanding of time scales in geophysics and palaeontology, as the objection to reversals of the field popularly held. Geological correlation in the Palaeozoic may be inaccurate and supposed contemporaneity may allow a difference of even tens of millions of years in age, during which the Pole might have moved fast enough to shift from one continent to another. In fact the South American glaciation is known to be earlier than and the Australian glaciation later than those of South Africa and India (du Toit 1954).

§ 18. The Hypothesis of Polar Wandering

Polar wandering seems to have been discounted by geologists and others on the vague feeling that it must somehow be easier to shift the continental rafts relative to one another than to move the earth. The problem of the dynamics of polar wandering has now been reopened with a less restricted earth model than Darwin (1877) used. In any sphere, rigid except for a ring of material which is caused to move through an angle θ_1, a marked spot on the surface will move through an angle θ_2 relative to a fixed point in space. θ is given by

$$\theta_2 = \frac{I_1}{I_2}\theta_1 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

by the conservation of angular momentum where I_1 is the moment of inertia of the ring about an axis perpendicular to its plane through its centre and I_2 the moment of inertia of the rest of the sphere about the same axis. The rapid rotation of the sphere about an axis perpendicular to this will not affect the situation but merely alter the reaction between the moving ring of matter and the sphere, so that the ring exerts on the sphere a torque about an axis perpendicular to the two mentioned above. This torque of course remains fixed relative to an axis in the body, and if the polar wandering is slow and the rotation fast it hardly affects the direction of the latter in space. On the contrary the effect of an external torque is to cause precession of the axis of rotation of the body in space.

Applying this to the earth it is necessary to estimate the additional torque required to alter the equatorial bulge. If the earth's crust was a continuous shell, a force to distort this to its new shape would be necessary, but a more realistic picture is that of a number of more or less loosely connected blocks floating on a plastic mantle. Thus the remodelling of the geoid consequent upon polar wandering must only overcome the friction between neighbouring blocks and the viscous resistance to flow in the mantle. This appears to be quite negligible.

Goguel (1950) and E. Fermi (private communication) have considered the possibility that marine currents, such as the Gulf Stream, may produce considerable polar wandering over geological time. Fermi rejected the possibility on quantitative grounds. It is however likely that even if there is a net angular momentum in the upper parts of the ocean it is likely to be compensated by an opposite angular momentum in the deeper ocean which cannot be so easily detected.

Vening Meinesz (1948) and H. Kuiper (1943) both consider the possibility of polar wandering occurring as a result of widespread convection in the mantle. However the latter is not definitely known to occur. Nevertheless it can be seen from eqn. (6) to be a very effective process. If the moment of inertia (I_1) of the convecting system in the mantle were one-fiftieth of that of the earth, then convective overturn must occur about 14 times to cause 90° of polar wandering. In 500 million years this implies velocities in the mantle of a few tens of centimetres a year. Such convection on such a long time scale is a very attractive explanation of polar wandering.

Gold (1955) has considered in some detail the instability of the earth's axis of rotation, resulting from the torques produced by the redistribution of mass on the earth's surface associated with tectonics, in particular mountain building. The free or Eulerian nutation of the earth, determined by astronomical observations of the variations of latitude, is apparently excited by random impulses but damped by at least 1 e of its amplitude in 10 periods (of 420 days). Bondi and Gold (1955) show that contrary to the view of Jeffreys (1952) the moment of inertia of the core is insufficient to cause this damping, from which it is therefore not possible to derive an upper limit for the viscosity of the core. They therefore assume that the mantle is, for slowly varying strains, inelastic and the necessary dissipation of energy occurs within it.

Gold argues that the restricted areas on the earth's surface where isostatic adjustment is not complete, and the very near equilibrium shape of the geoid in spite of changes in the rate of rotation of the earth due to tidal friction, point to an absence of permanent stiffness in the earth as a whole over geological times. If the earth was perfectly rigid the random impulses exciting the free nutation would build up its amplitude without limit.

Gold suggests that tectonic movements, representing the addition of an excess mass between the pole and equator would be effective in producing polar wandering. Gold estimates that if a continent of the size of South America was suddenly raised by 30 metres, an angle of 0·01° would in consequence separate the axis of fig. 20 from the axis of rotation and due to plastic flow polar wandering at a rate of 0·001° year would occur until the additional mass was situated on the equator. Gold estimates that large angles of polar wandering of the type envisaged above could occur in a million years.

§ 19. Conclusion

To summarize the position relating to reversals of magnetization we believe the following points to be of importance.

(1) Néel's prediction that self-reversal could occur in the iron oxide minerals on change of temperature by two different mechanisms has been strikingly demonstrated by Nagata on lava from Mount Haruna and by Gorter on a synthetic lithium fluoride.

(2) These mechanisms only account for reversals of magnetization in lava flows and other igneous bodies and only on the assumption that the iron oxides in the rock no longer possess this property, due to changes, chemical or structural, in them.

(3) No example has been found of a recent Quaternary rock reversely magnetized.

(4) In view of (3) and because it is becoming apparent that reversals occur with equal frequency both in igneous and stable sedimentary rocks, the most promising of the self-reversing mechanisms which Néel suggests is

that involving chemical or structural changes in the iron oxide minerals. However no physical or mineralogical difference between normal and reversed rocks has been demonstrated, except in the metamorphic rocks of the Adirondacks.

With regard to the interpretation of magnetizations widely different from the present earth's magnetic field, we might summarize the position as follows :

(1) Both igneous and sedimentary rocks older than the Tertiary are, where their stability can be proved, characterized by magnetizations remote from that of the present geomagnetic field.

(2) This mean magnetization, apart from reversals, tends to be constant throughout any geological epoch and over considerable distances.

(3) It might be suspected that the magnetization of sediments was considerably effected by prevailing river currents tending to orientate elongated iron oxide particles and by compaction during the early process of consolidation of the material into a rock. Nevertheless, where it is possible to compare the magnetization of lavas and sediments of the same age, general agreement between their directions of magnetization is found.

(4) Though in principle the establishment of stability on every rock measured is impossible, in practice the remanent magnetizations of rocks of the same lithology possess similar properties and proof of stability of rocks of the same type as those sampled for their palaeomagnetic properties is quite adequate.

(5) Measurements of directions of magnetizations of formations in different continents of the same or similar age give roughly the same positions for the magnetic poles in those ages. This world wide survey of palaeomagnetism is clearly however in a very rudimentary stage.

(6) Appreciable polar wandering seems indicated. There does not yet seem to be a need to invoke appreciable amounts of continental drift to explain the palaeomagnetic results so far obtained.

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References

Belshé, J. C., 1955, *Nature, Lond.*, in the press.

Blackett, P. M. S., 1952, *Phil. Trans.*, **245,** 309.

Bondi, H., and Gold, T., 1955, *M.N.R.A.S.*, in the press.

Bruckshaw, J. M., and Vincenz, S. A., 1954, *M.N.R.A.S.*, *Geophys. Suppl.*, **6,** 579.

Buddington, A. F., and Balsley, J., 1955, *J. Geomagn. and Geoelectr.*, in the press.

Bullard, E. C., and Gellman, H., 1954, *Phil. Trans. Roy. Soc.* A, **247,** 213.

Bullerwell, W., 1954, *Bull. Geological Survey of Gt Britain*, No. 6, 21.

Campbell, C. D., and Runcorn, S. K., 1955, in preparation.

Chevallier, R., 1925, *Ann. de Phys.*, **4,** 5.

Clegg, J. A., Almond, M., and Stubbs, P. H. S., 1954, *Phil. Mag.*, **45,** 583.

Cooke, H. B. S., 1953, *S.A. Journal of Science*, **50,** 123.

Creer, K. M., 1955, *Thesis*, Cambridge University.

Creer, K. M., Irving, E., and Runcorn, S. K., 1955, *J. Geomagn. and Geoelectr.*, in the press.

Darwin, G. H., 1877, *Phil. Trans.*, **167,** 271.

Du Bois, P. M., 1955, *Nature, Lond.*, in the press.

du Toit, A. L., 1954, *Geology of S. Africa*, 3rd Edit.,

Elsasser, W. M., 1946 a, *Phys. Rev.*, **69,** 106 ; 1946 b, *Ibid.*, **70,** 202 ; 1947, *Ibid.*, **72,** 821.

Fisher, R. A., 1953, *Proc. Roy. Soc.* A, **217,** 295.

Gelletich, H., 1937, *Beit. Angewand. Geophysik*, **6,** 337.

Goguel, J., 1950, *Ann. de Geophys.*, **6,** 139.

Gold, T., 1955, *Nature, Lond.*, **175,** 526.

Graham, J. W., 1949, *J. Geophys. Res.*, **54,** No. 2, 131 ; 1952, *Ibid.*, **57,** 429 ; 1953, *Ibid.*, **58,** No. 2, 243 ; 1954 a, *Ibid.*, **59,** 215 ; 1954 b, *Bull. Geol. Soc. Amer.*, **65,** 1257.

Griffiths, D. H., 1953, *Nature, Lond.*, **172,** 539 ; 1955, *M.N.R.A.S.*, *Geophys. Suppl.*, in the press.

Hallimond, A. F., and Butler, A. J., 1949, *Min. Mag.*, **80,** 265.

Heiland, C. A., 1930, *Zeit. f. Geophy.*, **6,** 228.

Hospers, J., 1951, *Nature, Lond.*, **168,** 1111 ; 1953, *Proc. Kon. Nederl. Akad. van Wetenschappen*, ser. B, **56,** No. 5, 467, 477 ; 1954, *Ibid.*, **57,** No. 1, 112.

Hospers, J., and Charlesworth, H. A. K., 1954, *M.N.R.A.S.*, *Geophys. Suppl.*, **7,** 32.

Irving, E., 1954, *Thesis*, Cambridge.

Ising, G., 1942, *Arkiv för Matematik, Astronomi, och Fysik*, Band 29A, No. 5, 1.

Jeffreys, H., 1952, *The Earth* (Cambridge : University Press).

Johnson, E. A., Murphy, T., and Torreson, O. W., 1948, *J. Terr. Mag.*, **53,** 349.

Johnson, E. A., Murphy, T., Michelsen, P. F., 1949, *Rev. Sci. Instr.*, **20,** No. 6, 429.

Kawai, N., 1951, *J. Geophys. Res.*, **56,** No. 1, 73 ; 1955, *J. Geomagn. and Geoelectr.*, in the press.

King, R. F., 1955, *M.N.R.A.S.*, *Geophys. Suppl.*, in the press.

Koenigsberger, J. G., 1938, *Terr. Mag.*, **43,** 119, 299.

Kuiper, H., 1943, *Poolbegegingen Tengevolge van Poolvluchtkracht* (Amsterdam).

Kumagai, N., and Kawai, N., 1955, *J. Geomagn. Geoelectr.*, in the press.

McNish, A. G., and Johnson, E. A., 1938, *Terr. Mag.*, **43,** 401.

Malamphy, M. C., 1940, *Trans. A.I.M.E.* (*Geophys.*), **138,** 134.

Mercanton, P. L., 1926, *Terr. Mag.*, **31,** 187.

Minakami, T., 1941, *Bull. Earth. Res. Inst.*, **19,** 363.

Nagata, T., 1953, *Rock Magnetism* (Tokyo).

Poole, G., Whetton, J. T., and Taylor, A., 1935, *Trans. Min. Met. Eng.*, **89,** 34.

Roche, A., 1950, *C.R. Acad. Sci.*, **230,** 113 ; 1951, *Ibid.*, **233,** 1132.

Runcorn, S. K., Benson, A. C., Moore, A. F., and Griffiths, D. H., 1951, *Phil. Trans.* A, **244,** 113.

Runcorn, S. K., 1954 a, *Trans. Amer. Geophys. Un.*, in the press ; 1954 b, *The Observatory*, **74,** 116 ; 1955, *Ann. de Geophys.*, in the press.

Rutten, M. G., and de Boer, J. C., 1954, *C.R.S., Soc. Geol. France*, **5,** 106.

Torreson, O. W., Murphy, T., and Graham, J. W., 1949, *J. Geophys. Res.*, **54,** No. 2, 111.

Vening Meinesz, F. A., 1948, *Gravity Expeditions at Sea*, IV (Delft).

Vincenz, S. A., 1954, *M.N.R.A.S., Geophys. Suppl.*, **6,** 590.

Wegener, A., 1912 a, *Petermanns Mitt.*, **185,** 253, 305 ; 1912 b, *Geol. Rundsch.*, **3,** IV, 276.

ERRATA

Electrons in Lattice Fields

By H. Fröhlich
Department of Theoretical Physics, University of Liverpool

Mr. G. R. Allcock has kindly informed me of a number of misprints in my article 'Electrons in Lattice Fields', *Advances in Physics*, 1954, **3**, 325.

In eqn. (5.29) delete the factor $(1/\epsilon_\infty - 1/\epsilon)$.

Replace eqn. (5.35) by

$$\dot{\Phi}_0(\mathbf{r}-\dot{\mathbf{r}}_0 t)=\Phi_0'\dot{r}_0\,; \quad \Phi_0'=-\frac{\dot{\mathbf{r}}_0}{\dot{r}_0}\frac{\partial \Phi_0}{\partial \mathbf{r}} \quad . \quad . \quad . \quad . \quad . \qquad (5.35)$$

Make replacements indicated by → in the following equations :

(5.36) $\mathbf{r}_0^{\,2} \rightarrow \dot{r}_0^{\,2}$
(5.40) $4\pi^2 \rightarrow (4\pi)^2$
(5.43) $8 \rightarrow 48$
(5.44) $\frac{1}{2} \rightarrow \frac{1}{12}$

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